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Chelating polymers :

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CHELATING POLYMERS : THEIR PROPERTIES AND APPLICATIONS IN RELATION TO REMOVAL, RECOVERY AND SEPARATION OF TOXIC METAL CATIONS

By

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ABSTRACT

More than 60 million metric tons of hazardous wastes are generated annually throughout the United States of which little higher than 60% is generated by chemical and allied industries. Approxiamtely 60% of the hazardous waste is liquid or sludge; and most of them are disposed of on the generators' property. Rainfall causes infiltration and/or runoff to occur. Infiltration allows the transport of hazardous waste into groundwater supplies, and surface runoff leads to the contamination of streams or lakes. Major aquifers and well withdrawals underlie areas where the wastes are generated. Thus the hazardous waste problem is compounded by two considerations: the wastes are generated and disposed of in areas where it rains and in areas where people rely on aquifers, streams or lakes for the supplies of drinking water. Previously, major ground water or surface water problems resulted from agricultural activity; contaminants were predominantly nitrate and other inorganics. More recently, however, widespread contamination of usable groundwater aquifers and streams by synthetic organic chemicals and toxic metals, resulting from landfill leachates and other non-point sources, has raised concerns for an irreparable degradation of nation's drinking water sources.

Potential of the chelating ion exchange resins for the individual separation and recovery of the toxic metal cations, namely, cadmium, copper, nickel, lead and zinc, has been investigated in the present study so that the recovered metals can be recycled for beneficial use in accordance with the basic philosophy of the Federal Resource Conservation and Recovery Act (RCRA). Chelating polymers are essentially copolymers with covalently bound immobilized side chains containing one or multiple donor atoms (Lewis Bases)

which form coordinate bonds with toxic metal ions (Lewis Acids). Due to this bonding, the chelating copolymers exhibit a high affinity for toxic metal ions compared to alkali metal (sodium, potassium, etc.) and alkaline earth metal (calcium, magnesium, etc.) cations which are inevitably present in water at several orders of magnitude greater concentrations. Specifically, this study is aimed at investigating the effects of (i) type of functionality in the chelating copolymer, (ii) aqueous phase pH, and (iii) aqueous phase ligand (ethylenediamine) concentrations in order to recover and separate toxic metal ions from contaminated water sources.

Chapter 1
INTRODUCTION

1.1 WATER RESOURCES AND TOXIC CHEMICALS

Late in the summer of 1978 the name of a small residential subdivision in the city of Niagara Falls, New York, became a household word almost overnight, symbolizing the dangers of the chemical age. The tragic sequence of events which unfolded at Love Canal epitomizes the dangers facing millions of citizens in thousands of communities across the nation as a result of the indiscriminate use and careless disposal of hazardous chemicals. While Love Canal has dominated media reports focusing hazardous waste problems, a large and still growing number of other horror facts highlight the diversity of chemical waste situations and thereby contamination of the nation's drinking water through infiltration and surface runoff [2].

For centuries, chemical wastes have been the necessary by-products of developing societies. Here a disposal site, there a disposal site, everywhere a disposal site - all with little or no attention to potential impacts on ground water quality, runoff to streams or lakes. Engineering decisions here historically were made by default; dumping these waste products "out back". Historically, the largest percentage of toxic wastes have been disposed of on land, primarily because land disposal was by far the cheapest disposal option. During the mid-1970s, almost half of all toxic and hazardous wastes were simply dumped into unlined surface impoundments, technically referred to as "pits, ponds, or

lagoons", located on the generators' property. These wastes eventually evaporated or percolated into the soil, often resulting in ground water contamination; or washed away with surface runoff to contaminate the nearby lakes and streams [61]. Awareness about heavy metal contamination of water resources grew fairly slowly, because most of the heavy metal cations are fairly immobile due to their low solubility at neutral to alkaline pH. However, acid rain, the presence of natural and synthetic organic ligands in percolating water, periodic high chloride concentrations (chloride is an inorganic ligand) during salt spraying for deicing in the winter - all accelerated the mobility of the toxic metal ions from the solid wastes and "dumps". Characteristics of such toxic metal ions with regard to their speciation, mobility, biodegradability and interactions with naturally occuring humic and fulvic acids have been studied by others [51]. Since Maximum Contaminant Levels (MCL) for all such toxic metals in drinking water are in the micro-gram level, according to Safe Drinking Water Act (SDWA), detoxifying the sources of such contamination is an approach in the right direction. More importantly, all such toxic metals are useful with high commercial value provided they can be recovered and separated.

Chelating ion exchange resins have high affinity for metal ions. These resins can be used to remove the metals present in a drinking water supply or in a waste at the generators' site to curb their journey from the generators' site to a potential drinking water source, like aquifers and streams. Due to their high capacity and selectivity for bivalent and transition metals, chelating ion exchange resins can be used to recover the metals from alkali or alkaline earth metal containing wastes. These selective resins have potential in the removal of precious metals from base metals; treatment of waste waters; treatment of effluents from nuclear installations and novel separation of metals. However,

the regeneration effluent from these resins contains a very high concentration of various toxic metals. The only solution to handle this concentrated metal bearing regenerated waste effluent is to separate and recover individually the metals present, so that the metals can be recycled for beneficial use. The present study is an attempt to address some scientific aspects for such a global solution.

1.2 ION EXCHANGE RESINS AND EMERGENCE OF CHELATING POLYMERS

The papers of Thompson and Way, now a hundred years old, are classics in soil science and in general chemistry, the work of Gans and the widespread use of synthetic zeolites for water softening provide another familiar landmark. Important works in the field of zeolites were done by Barrer [3, 4]. Their practical use is beset by limitations, however, and the great developments of recent years in the use of ion exchange are due almost entirely to the organic exchangers now available.

The organic ion exchange resins were first prepared and studied by B. A. Adams and E. Leighton Holmes at the Chemical Research Laboratory, London, and described by them in a paper read before the London Section of the Society of Chemical Industry in December 1934 and published in the Transactions for 1935. Ion exchange resins have undergone drastic diversification and improvements since then and are extensively used for softening or completely deionizing water, for removing impurities, for recovering valuable materials present in small concentrations, for the separation of ions and for preparing new materials.

Exchangers are available which behave as insoluble strong acids, strong bases, weak acid or weak bases. Those based on polystyrene are very stable and

chemically inert. A major difference in the behaviour of strong and weak exchangers is that whereas the former are freely permeable to ions so that exchange is a quite rapid process; with weak exchangers this is only true of the ionized forms i.e., of weak acids at high pH or weak bases at low pH. An exchanger with weakly ionized acid e.g. carboxylic acid will be almost unionized and will swell little in dilute acid solution and when the pH is raised its complete penetration by cations from the solution will require hours rather than minutes which are observed in the case of strong acid or base exchangers.

The selectivity of an ion exchange resin for different ions may be increased by increasing the degree of cross linking in the resin [48]. However, this great increase in selectivity will be obtained at the expense of a decrease in exchange rates. For the preparation of resins showing increased selectivity, modifications in the chemical structure, in particular in the nature of the exchange sites have been preferred to modifications in the porosity of resin. Resins containing functional groups possessing chelating or complexing properties show greatly increased selectivity which need not neseccarily be obtained at the expense of a reduction in exchange rate [48].

The preparation of resins containing active groups showing specific or selective behaviour towards metallic cations has stemmed from the above concept of incorporating, within the resin, a functional group which can form chelate or co-ordinating complexes with the metal ions. Skogseid [52] was the first to prepare a chelating resin by causing picryl chloride to react with nitrated and reduced polystyrene and then nitrating the product. The resultant chelating resin, thus produced, behaved as a cation exchange resin with an affinity of potassium several times greater than that shown by conventional cation-exchange resins. Gindin [20] and coworkers have examined the extraction of metal ions using carboxylic acids (C_7-C_9 fatty acids). They found

that the degree of extraction depended on the pH value of the aqueous phase and the basicity of the metal ions. Contrary to the conclusion of Gindin, Flett [18] observed marked effects of anion on the metal extraction with naphthenic acid (cyclopentyl alkylcarboxylic acids).

1.3 OBJECTIVE AND SCOPE OF STUDY :

The donor atoms, present in the covalently attached side chains of chelating polymers, bind the metal ions into the resin macromolecule through coordinate covalent bonding. As observed from Fig. 1-1, the bond energy involved in chelation reaction [32] is, in general, within reversible range making the desorption of previously adsorbed metal ions on to chelating polymers, with acid or alkali, quite efficient. The adsorption and desorption of metal ions, on to and from the cheating resin respectively, can be represented as :

$$2RH + M^{2+} = MR_2 + 2H^+ \quad \text{(Adsorption Reaction)} \qquad (1.1)$$

$$MR_2 + 2HCl = 2RH + MCl_2 \quad \text{(Desorption Reaction)} \qquad (1.2)$$

Where, RH = Hydrogen form of the resin, M = The target metal ion to be recovered, MR_2 = The chelated metal-polymer complex, and HCl = Hydrochloric acid used for the resin regeneration.

The objective of the present study is primarily aimed at separation and recovery of divalent metal cations from a waste containing cadmium, copper, nickel, lead and zinc using chelating polymers. The high metal removal capacity (given by Eq. (1.1)) coupled with extremely high acid/alkali elution efficiency (given by Eq. (1.2)) of chelating polymers indicate their advantages over conventional ion exchange resins for the separation and recovery of metals.

The effect of the donor atoms, incorporated into the resin functional group,

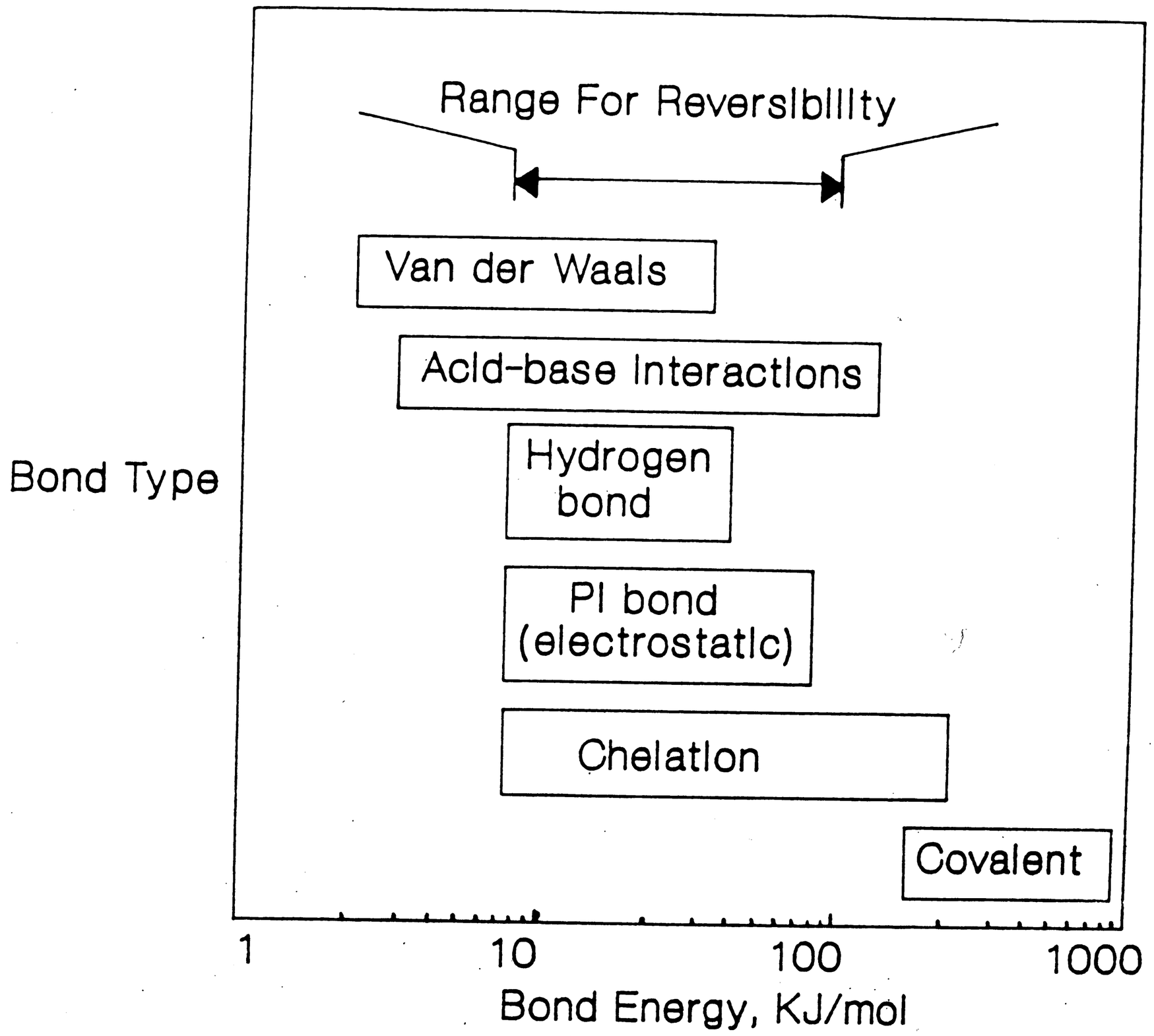


Figure 1-1: Bond Type vs. Bond Energy of Different Types of Physical/Chemical Interactions [32]

on the separation of the five metals has also been addressed in this study. Resins DP-1 and Bio-Rex 70, obtained from Rohm and Haas and Bio-Rad respectively, contain carboxylate functional group with oxygen donor atoms (chemical structure given in Fig. 2-1). Resin XFS-4195, obtained from Dow chemicals, has pyridine functional groups with three nitrogen donor atoms (for chemical structure ref. Fig. 2-5). Resin GT-73, obtained from Rohm and Haas, has thiol functional group (chemical structure given in Fig. 2-6) with one sulfur donor atom. Resins IRC-718 and Chelex-100, manufactured by Rohm and Haas and Bio-Rad respectively, have iminodiacetate functional group with multiple donor atoms; one nitrogen and two oxygen atoms (chemical structure given in Fig. 2-7).

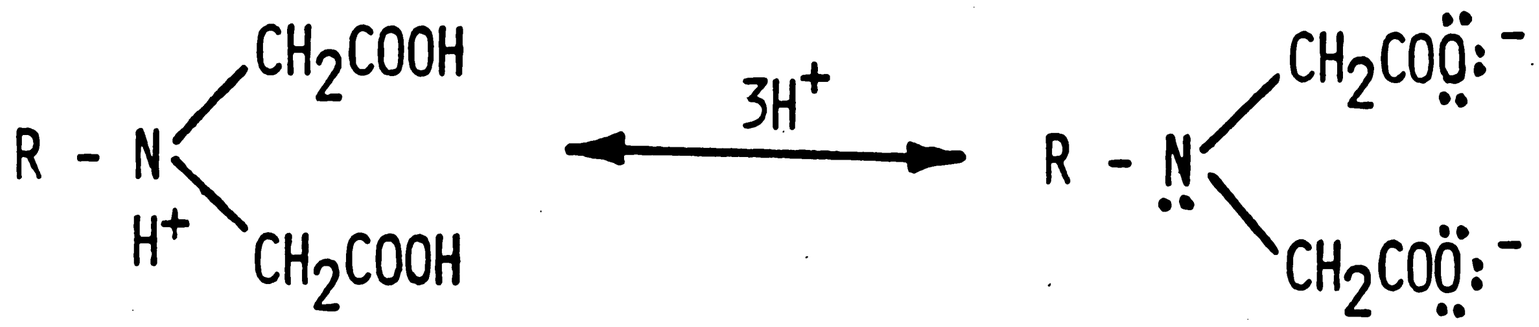
All the above resins are weakly acidic (DP-1, Bio-Rex 70, GT-73, IRC-718 and Chelex-100) and/or weakly basic (XFS-4195) in nature; and Fig. 1-2 shows the protolysis reactions along with individual donor atoms for these immobilized functional groups. It is observed from Eq. (1.1) that during adsorption or chelation of metal ions on to the resin, equivalent amount of hydrogen ions are generated into the system. Due to the weakly ionizing nature of the resins studied, it can be anticipated that the generated hydrogen ions will influence the metal removal capacity and selectivity. Hence, for each of the four chelating resins, studies are also made to enhance the separation and recovery of the target metals by varying the aqueous phase pH.

In the metal-copolymer reaction, given in Eq. (1.1), the polymer acts as a Lewis Base with the donor atoms loosing their electrons. The adsorbing metal ions act as Lewis Acids accepting the electrons from the donor atoms. The presence of a stronger ligand with a high electronegativity or electron donation capability in the aqueous phase will shift the metal-polymer chelation reaction to the metal-ligand chelation. Studies are made with the deliberate addition of

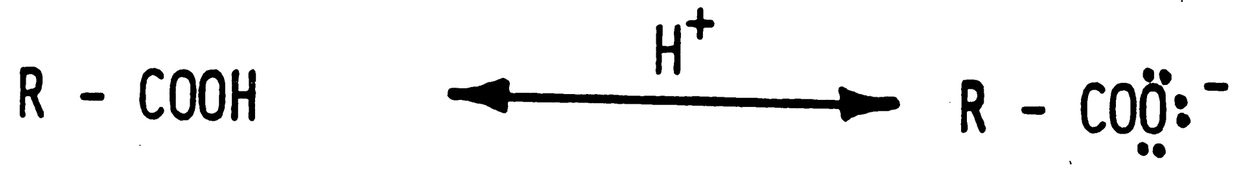
ethylenediamine, a bidentate ligand, into the system to modify the separation factor of a given resin (DP-1) in order to enhance the separation and recovery of the target metals.

IMPORTANT FUNCTIONALITIES

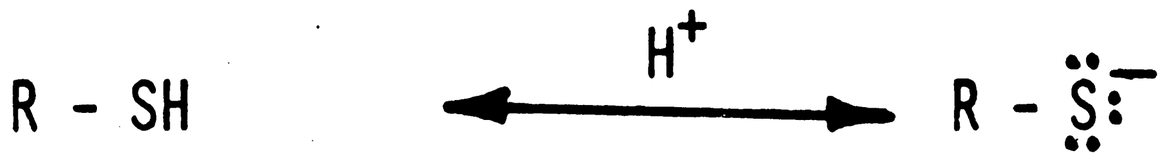
IMINODIACETATE (IRC-718 and Chelex-100):



CARBOXYLATE (DP-1 and Bio-Rex 70):



THIOL (GT-73):



TERTIARY AMINE AND PYRIDINE (XFS-4195):

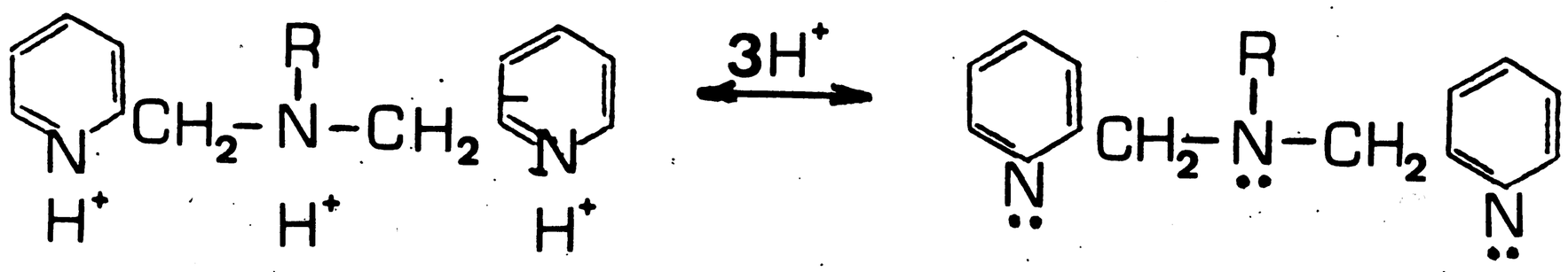


Figure 1-2: Chelating Ion Exchange Resin Functionalities with the Donor Atoms and their Protolysis

Chapter 2
CHELATING ION EXCHANGE RESINS AND METAL ION SELECTIVITIES

2.1 ION EXCHANGE RESINS

Most ion exchange resins in commercial use today are based on an organic polymeric network although inorganic polymers may be used. Irrespective of the composition network, the basic function of the polymeric network is to limit the solubility of resin. The chemical nature of the polymeric network is a major factor in determining the physical and chemical character, stability and property of the resin.

Most ion exchange resins contain styrene and divinylbenzene (DVB) as the base polymer. When styrene is polymerized, the resulting macromolecular compound becomes a straight chain compound and it is essentially one dimensional. The function of DVB, when added into the polymerization mixture, is to interconnect at more or less regular interval the polymerized straight chain styrene molecules. The resulting structure becomes three dimensional or cross-linked. The DVB is called as crosslinker in the process of polymerization.

When a crosslinked polymer is placed in an organic solvent, it will try to dissolve like the linear polymer. However, dispersion will stop when the osmotic force of solvation will be counterbalanced by the internal stress developed by the stretched polymeric network. The higher the amount of DVB in the monomer

mixture, i.e., more the degree of crosslinking in the resin, the smaller will be the solvent picked up by the resin.

2.1.1 Resin Functional Groups

Functional groups are the fixed ion exchange sites of the styrene-DVB copolymers. These ionic sites are attached to the copolymeric network by one or more chemical reactions and impart ion exchange properties to the polymer. Besides, these ionic sites convert the organic-swellable copolymer into a water-swellable material. Each ion exchange resin is characterized by its fixed ionic sites or functional groups. To a great extent, the process of separation of dissolved constituents from one another, is dependent on the functional groups attached to the ion exchange resins. The degree and the order of separation can be altered by changing the functional groups in the ion exchange resins.

2.1.2 Counterions and Co-ions

To maintain electrical neutrality of the system, the charges due to the fixed ionic sites in the resin structure are balanced by a like number of ions of opposite charges. These ions are called counterions. True ion exchange process is the transfer of counterions from the external liquid phase to the internal solid phase of resin. Such ion exchange is always on an equivalent basis; that is, the same number of ionic charges leaves the inside phase as simultaneouly enters into it. Exception to this rule of equivalency of exchange is observed when ion exchange is accompanied by chemical reactions, formation of a precipitate or formation of a poorly ionised component which is physically adsorbed by the resin.

Ions having the same sign as the functional groups of resin are called co-ions. When the ionic concentration of the outside liquid phase is low, the co-ion concentration in the inside solid phase may be negligible. Increasing the external concentration, will increase the co-ion concentration inside the resin.

An ion exchange process is essentially a heterogeneous process. The dissolved component or constituent leaves the external liquid phase and goes into the inside solid phase of resin where it is adsorbed and thereby gets separated or removed.

2.1.3 Separation Factor

Separation factor is a surrogated parameter which indicates the preference of ion exchange resin of one ion above the another. An ion exchange reaction can be represented as:

$$RA + B = RB + A \tag{2.1}$$

Where, ion B from the outside liquid phase is displacing the ion A from the exchanger phase.

From the reaction given in Eq. (2.1) above, the separation factor of a resin for the ion B with respect to ion A can be given as [36, 38, 45, 33] :

$$K_A^B = \frac{[RB][A]}{[RA][B]} \tag{2.2}$$

Where,

K_A^B = Separation factorof ion B over A

RA = Resin phase concentration of ion A

RB = Resin phase concentration of ion B

A = Aqueous phase concentration of ion A

and

B = Aqueous phase concentration of ion B.

If Q is defined as the total ion exchange capacity of the resin and C_T as the total aqueous phase concentration, dividing both the numerator and denominator of Eq. (2.2) by Q and C_T results :

$$K_A^B = \frac{Y_B X_A}{Y_A X_B} \tag{2.3}$$

Where,

$Y_A = \frac{[RA]}{Q}$ = Resin phase fraction of ion A

$Y_B = \frac{[RB]}{Q}$ = Resin phase fraction of ion B

$X_A = \frac{[A]}{C_T}$ = Aqueous phase fraction of ion A, and,

$X_B = \frac{[B]}{C_T}$ = Aqueous phase fraction of ion B.

The terms $\frac{Y_A}{X_A}$ and $\frac{Y_B}{X_B}$ are known as selectivities of ion exchange resin for the ions A and B respectively. The separation factor and selectivity have to be greater than unity to obtain a favorable condition for good separation.

2.1.4 General Characteristics

Fundamental studies of the behaviour of ion exchange resins have established certain important features of the ion exchange process and the following generalizations may be made :

(a)*Ion exchange reactions are stoichiometric*

That is for every g.equiv. of the exchanging ion B taken up by the resin, a g.equiv. of the ion A is liberated in the solution unless this equivalence of exchange is obscured by other effects like formation of a precipitate or exchanging is accompanied by chemical reaction.

(b)*Ion exchange reactions are, in general, reversible*

In the reaction given by Eq. (2.1), the forward reaction will only approach completion if the resin adsorbs B much more strongly than A or if there is a large excess of B ions relative to the A ions liberated to the solution. The forward reaction will also proceed more readily if A ions are removed from the system through the formation of an incompletely dissociated compound, e.g. by complex formation.

(c)*Ion exchange resins show no exchange hysteresis*

The ionic composition of a resin, in equilibrium with a given solution, is always the same irrespective of the direction in which equilibrium is approached. Where hysteresis is apparently observed, this may be due to the failure to attain equilibrium or to the changes in the structure of the resin.

(d)*All the acidic (or basic) groups in an ion exchange resin are accessible as exchange sites for small ions*

The total exchange capacity, expressed in g.equiv., is therefore the same for all small ions and is quite independent of particle size. The full capacity of the resin is determined simply by the number of ionized groups per unit mass or volume.

As a consequence of high proportion of polar groups in their structure, ion exchange resins are strongly hydrophilic, complete solubility in water being prevented by the cross-linked network. They behave as hygroscopic gels, swelling and shrinking reversibly with adsorption and desorption of moisture.

2.1.5 Effects of the Degree of Cross-Linking

The behaviour of a given type of ion exchange resin can be modified by varying the degree of cross linking of the polymeric network. With the cross linked polystyrene resins, this can be achieved by varying the proportion of DVB used in the preparation of the copolymer. In particular, the degree of cross linking has a marked influence on the swelling in water, the exchange rates, the relative affinities and non-exchange behaviour such as adsorption of electrolytes and non-electrolytes.

As the proportion of DVB is decreased, the swelling of the resin increases rapidly and the capacity per unit volume decreases. Since for most applications a high exchange capacity per unit volume is required, it would be advantageous to use highly crosslinked resins with low swelling in water. The choice of the degree of cross linking of commercial resins usually involves a compromise because of the effect on the rates of exchange.

Under conditions where particle diffusion is rate controlling, the degree of cross linking has a marked effect on the rate of exchange. As the degree of cross linking is increased the exchange rate decrease. Increased cross linking reduces the rate of exchange by reducing the amount of water available as a diffusion medium [36, 26, 48].

The ability of resins to discriminate between different ions is also greatly influenced by the extent of cross linking. Resins of very low crosslinking are non selective; but if the degree of cross linking is increased, the selectivity increases considerably [36, 48].

2.2 CHELATING ION EXCHANGE RESINS

The selectivity of an ion exchange resin for different ions may be increased significantly by increasing the degree of crosslinking in the resin [48]. However, it is apparent from the above that any great increase in selectivity will be obtained at the expense of a decrease in exchange rates. The development of chelating ion exchange resins has originated from the concept of incorporating into the resin matrix a functional group, which has chelating or complexing properties for a specific ion or a group of ions, such that a high resin specificity or affinity is observed for that particular ion or group of ions without increasing the degree of cross linking and consequent sacrifice of exchange rates [48].

The chelating ion exchange resins are copolymers with covalently bound side chains which contain one or more donor atoms that are able to form coordinate covalent bond to a metal and this coordination is frequently accomplished by ion exchange. The first of such resins prepared was the dipicrylamine resin [52] which is specific for the potassium ion. Most chelating resins contain nitrogen, oxygen or sulfur atoms or a suitable combination of these atoms in the resin active sites or functional groups [21, 22]. In general, chelating ion exchange resins are weakly ionised resins, weakly acidic or weakly basic in nature, and therefore the rate controlling process is the particle diffusion of hydrogen ions [12].

Four types of widely used commercial chelating resins have been studied along with five metals namely, cadmium, copper, nickel, lead and zinc. The first one contains mono-carboxylic acid functional groups with oxygen as the donor atoms. The second one contains pyridine as the functional groups with the nitrogen as the donor atoms. The third one contains the thiol groups into the resin active sites with sulfur as the donor atoms. The fourth one contains imino-diacetate functional groups with both nitrogen and oxygen as the donor

atoms. The ion exchange capacities of these resins vary from negligible capacity to a high exchange capacity depending on the pH of the solution with which they are in equilibrium. These weakly ionised resins form strong complexes with the metal ions and are extensively used in mineral recovery. The functionalities of these chelating resins are designed to have high specificity for bivalent and transition metals.

2.2.1 Resin with Monocarboxylic Functionality (DP-1, Bio-Rex 70)

A monofunctional carboxylic resin can be prepared by the copolymerization of methacrylic acid with divinylbenzene (5-10%) in the presence of 1% benzoyl peroxide. The preparation and the basic chemical structure of polymethacrylic acid-DVB (DP-1 and Bio-Rex 70) resin is given in Fig. 2-1.

There are few aromatic rings in the resin structure and the carboxylic acid group (-COOH) itself represents a high percentage of the total solids in the resin. The -COOH is the functional group or ion exchange site in this resin. In an ion exchange reaction, the functional group exchanges the hydrogen ion (H^+) with the ion to be removed or recovered. Because of the presence of a high number functional groups in the copolymer, this resin has a high ion exchange capacity per gram of solid when fully ionised at high pH. The pK_a value of this resin appears to be dependent on the degree of crosslinking (DVB content) and the external aqueous phase concentration in which the resin is equilibrated [27, 36]). An increase in the DVB content increases the pK_a value; in contrast, an increase in the aqueous phase concentration decreases the pK_a value.

Carboxylic acids dimerize in organic solvents. The favoured structure for the dimer is a planar cyclic hydrogen bonded species [47]. The dimerized cyclic

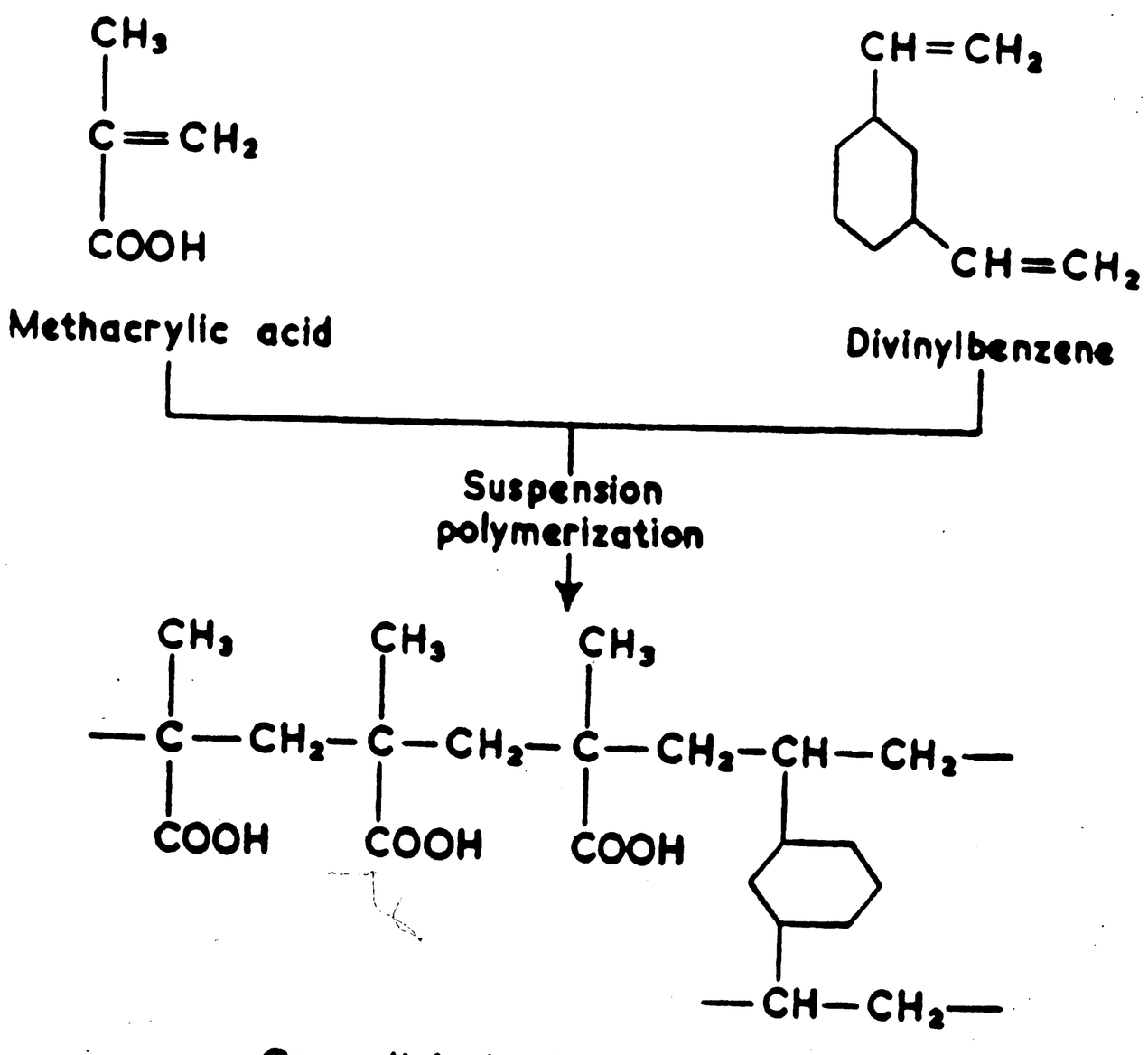


Figure 2-1: Preparation and Chemical Structure of Carboxylate Resin

structure of carboxylates, as suggested by Pauling and Brockway, is presented in Fig. 2-2 along with bond angles and bond lengths of the carboxylates. As shown in Figure 2-3 carboxylic acids have two resonance forms, which give equivalent ions. Owing to the equivalence of two resonating forms, carboxylate ions are stabilized to a greater extent than free carboxylic acids, for which resonating forms are not equivalent. The C - O bond lengths, therefore, identical (1.26^0A) in carboxylate ions and the heats of combustion show the resonance energy to be approximately 28 kcal mol^{-1}.

In aqueous solution, carboxylic acids tend to dimerize in the open form (ref. Fig. 2-4) and not in the cyclic form (ref. Fig. 2-2) which is observed in the solid and vapour states, and in non-ionizing solvents. Ionization or dissociation of these acids produces a resonance stabilized carboxylate anion and a hydrated proton. While most carboxylic acids have a pK_a value of approxiamtely 4.8, any substituent on R, which tends to stabilize the carboxylate anion by electron withdrawl, will increase the acidity and lower the pK_a.

A large volume of work on the extraction of metal ions with carboxylic acids has been carried out in the USSR, mostly on the commercially available acids. The studies of Gindin and his coworkers [20] have permitted the compilation of selectivity series for the extraction of metal ions by carboxylates :

Sn(IV) > Bi(III) > Fe(III) > Ti(III) > Sb(III) > Pb(II) > Ga(III) > Cr(III) > In(III) > Cu(II) > Al(III) > Y(III) > Ce(III) > Ag(I) > La(III) > Cd(II) > Zn(II) > Ca(II) > Ba(II) > Ni(II) > Cs(I) > Rb(I) > K(I) > Co(II) > Mn(II) > Mg(II) > Na(I)

Thus, from the selectivity series given above, any metal present in the aqueous phase will displace all those metals to the right of it in the series from the

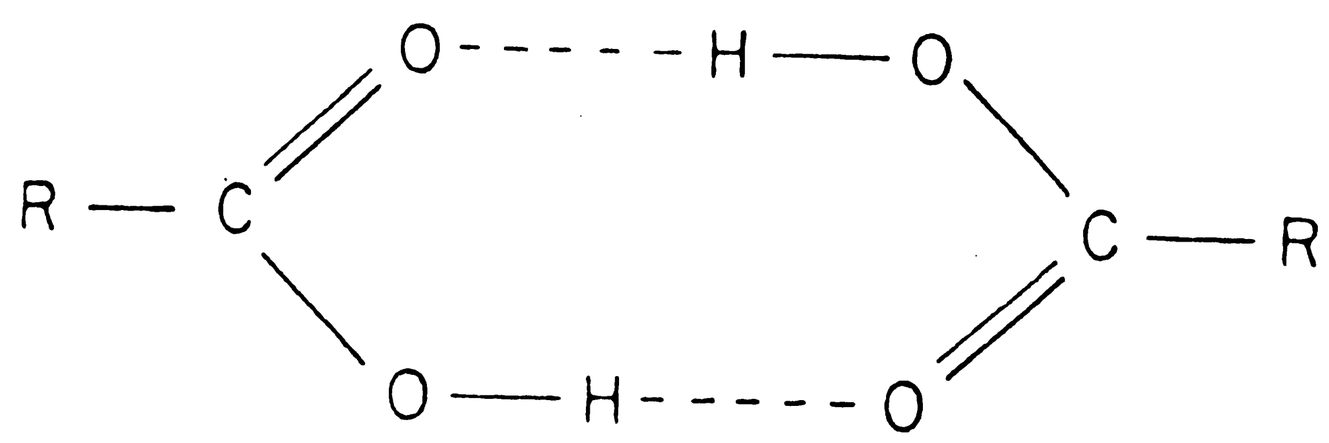
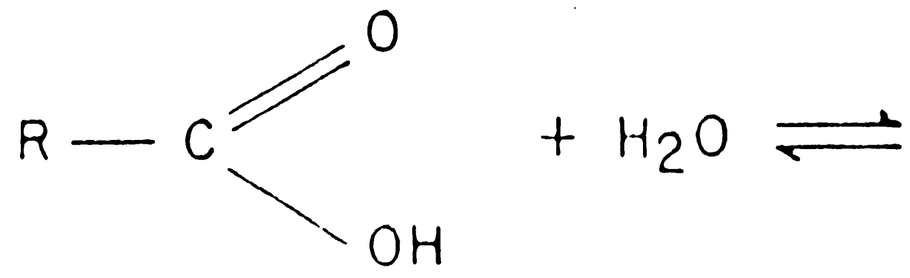


Figure 2-2: Cyclic Structure of $(RCOOH)_2$



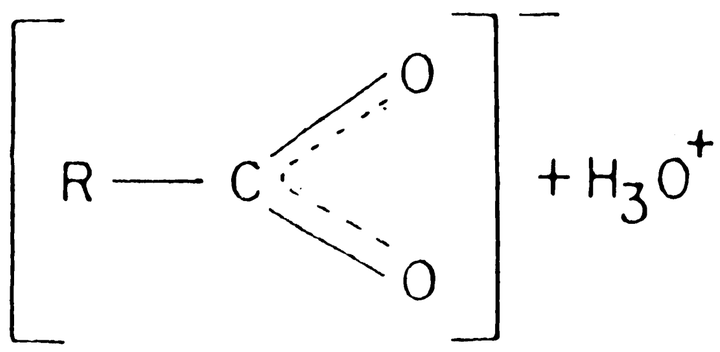


Figure 2-3: Resonating Forms of Carboxylates

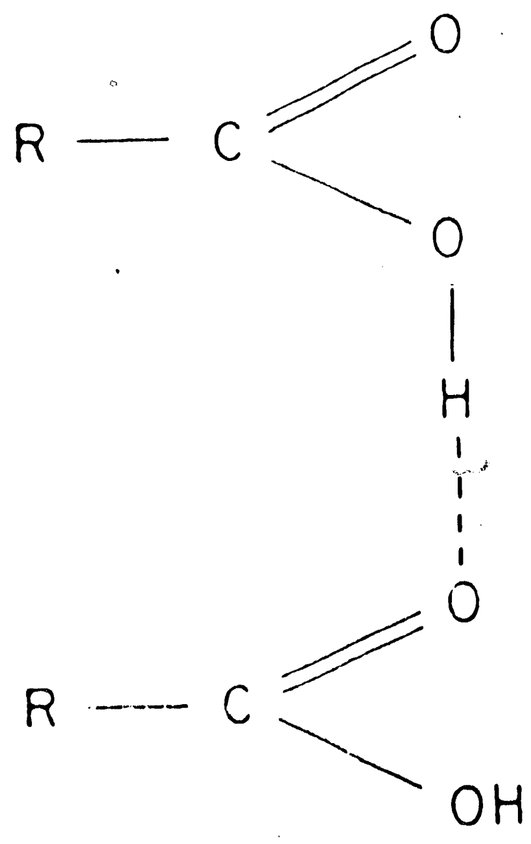


Figure 2-4: Open Form of $(RCOOH)_2$

corresponding metal carboxylates in the organic phase. The low acidity of the carboxylic acid resins is undoubtedly the result of the ability of the carboxylic acid groups to form covalent bonds with hydrogen ions and one can assume that the ability to form covalent bonds with one ion could be extended to other ions capable of forming covalent bonds. The selectivity series given above, in general, is in the decrasing order of the covalent bond forming ability of the metal ions.

2.2.2 Resin with Nitrogen Donor Atoms (XFS-4195)

This is a wealkly basic macroporous resin with polystyrene matrix and divinylbenzene cross linking to which has been attached a chelating functional group consisting of two pyridine molecules and one tertiary amine group. The chemical structure of this resin is presented in Fig. 2-5.

This resin has a pK value approximately 4.5 and exhibits a high selectivity for the transition group metals like copper and nickel [22].

2.2.3 Resin with Sulfur Donor Atoms (GT-73)

The chemical structure of this resin resin is presented in Fig. 2-6. This resin shows a high selectivity for mercury (Hg) and is long being used for the recovery of mercury from contaminated waste. This is also a macroporous resin with polystyrene matrix and divinylbenzene crosslinking with the thiol (SH) groups as the active sites.

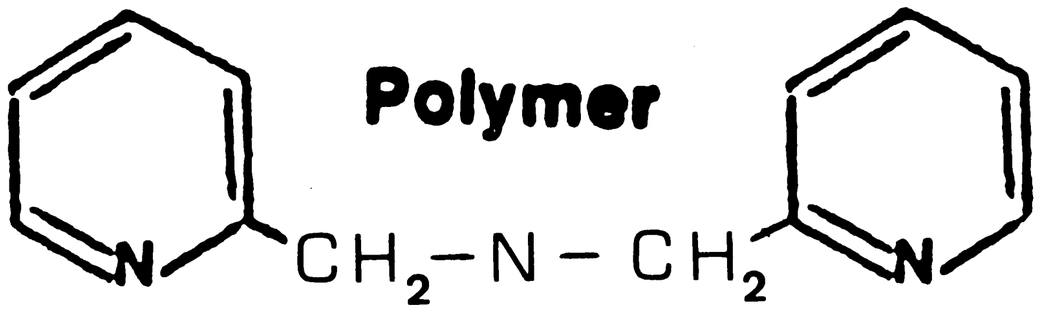


Figure 2-5: Chemical Structure of Resin XFS-4195

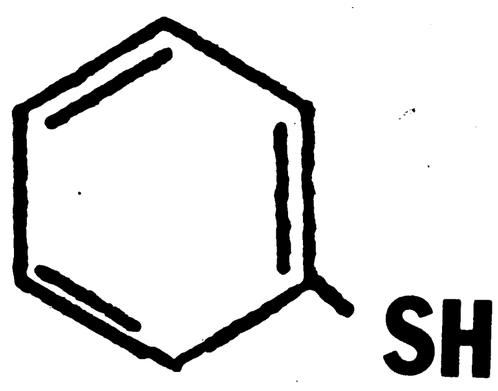


Figure 2-6: Chemical Structure of Resin GT-73

2.2.4 Resin with Iminodiacetate Functionality(IRC-718, CHELEX-100)

This resin is made from styrene and DVB through a number of synthesis steps. The functional group of this resin is $-N(CH_2COOH)_2$; and is analogous to ethylenediamine tetracetic acid (EDTA). This resin has been made commercially since the 1950s and similar resins are available from several resin manufacturers. The idealized structure of this type of resin is given in Fig. 2-7.

The method of preparation of this type of chelating resin is the reaction of the chloromethylated copolymer with iminodiacetonitrile, followed by hydrolysis of the product.

$$R.CH_2Cl + NH(CH_2.CN_2) \rightarrow RCH_2.N(CH_2.CN)_2 \rightarrow R.CH_2.N(CH_2.CO_2H)_2$$

Resins prepared by this method have shown to possess a high affinity for copper and other bivalent transition metals. The iminodiacetate structure of this resin forms strong complexes with a wide variety of di- and trivalent cations. Selectivity of this resin, for various cations, follows the same general pattern as the complex stability constants of EDTA in solution. However, the incorporation of the functional group in a crosslinked polymer matrix puts limitation on the behaviour. The reaction mechanism of the iminodiacetate group is dependent on the cation present in aqueous phase. In the case of transition group metals, like copper and nickel, an additional reaction of Lewis Acid-Base type takes place between the N atom in the functional group and the metal ions [28, 1, 39]. Due to the presence of nitrogen and oxygen donor atoms in the resin functional group, resin of this type is expected to posses both cation

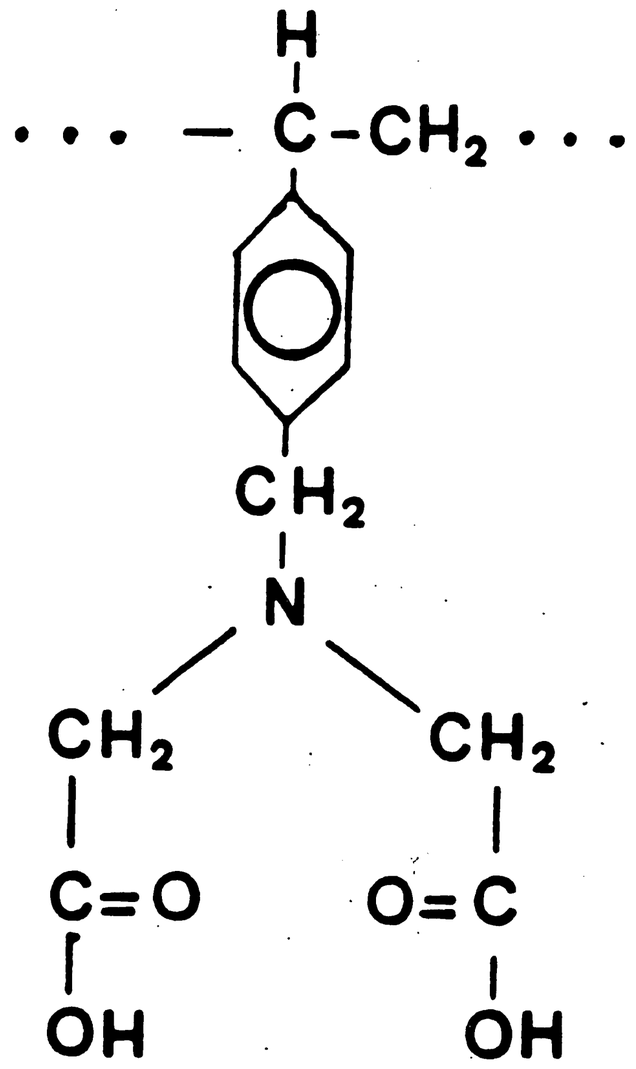


Figure 2-7: Chemical Structure of Resin with Iminodiacetate Functionality

and anion exchange characteristics and the metals which form strong covalent bond with donor nitrogen atom, like copper or nickel, will be more preferably adsorbed by this resin.

Diaz et.al. have reported four pK values for resin with iminidiacetate functionality [14]. However, Marinsky [35] observed the pK value of 2.77 for this type of resin. This pK value of Marinsky is in agreement with the pK value of 2.54 observed by Martell et.al. [10] for iminodiacetic acid.

2.3 Experimental Determination of Separation Factors for Metal Ions

The experimental method consisted of equilibrating the resins, namely, DP-1, XFS-4195, GT-73 and IRC-718 resin in small glass columns at different pH conditions but with the same aqueous phase composition. All the resins were preconditioned and were in Ca form except XFS-4195. The resin XFS-4195 was in nitrate form. The feed water with constant composition was passed through the resin columns for about four months and the effluent pH, at all the column outlets, was observed same as that of inlet. The column feed consisted of 500 mg/l of Ca^{2+} ion and about 0.1 mg/l each of Cd^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+} ions. The metal ions concentration was kept very low for the following reasons:

(a) The maximum concentration of metal ions in aqueous phase is dependent on pH. The maximum pH used in the study was 6.52. Among the five metals studied, at a given pH, lead has the lowest solubility. The solubility of Pb^{2+} ion in aueous phase at pH of 7.0 is 0.294 mg/l. To avoid metal hydroxide precipitation on the resin and to be on the conservative side, the metal ions concentration was kept below this limiting value. The detailes of the speciation of metals in aqueous phase is given in Appendix L.

(b) The objective of the study was to determine separation factor of individual metal ions with respect to calcium at a definite pH condition. When the aqueous phase concentration of an ion is very low, the ion behaves as a "trace species". Under this situation, the competition among the metal ions for the same ion exchange sites can be ignored. In an ion exchange reaction with trace species, the separation factor of individual ions with respect to the bulk species are not affected by the presence of other species [26].

2.3.1 Metal Ion Separation Factor with Carboxylate Resin

The K_{Ca2+}^{M2+}, separation factors of the metal ions with respect to calcium are presented in Table 2-1 and also in Fig. 2-8 at a pH of 4.1 and 6.52. The capcity of the resin was found as 0.347 meq/gm and 5.794 meq/gm at a pH of 4.1 and 6.52 respectively. Appendix A and Appendix B form the basis of calculation of the metal ion separation factors for the carboxylate resins. The separation factors of metal ions, given in Table 2-1, have been rounded to the nearest integer value.

Except nickel ion, the separation factor with respect to calcium of all the metal ions increased as the equilibrium pH was increased. However, the increase in separation factor with pH varies among the metal ions studied. The cadmium ion undergoes an increase of about 40 times in separation factor; and, the separation factor of copper ion improves by about 20 times. The separation factor of zinc ion increases by about 3 fold. The increment in separation factor for the lead ion is about 1.25 times. The separation factor of the nickel ion remains practically unaltered at both the equilibrated pH conditions. Based on the decreasing separation factor, the different metal ions for the carboxylate resin can be ranked as :

Table 2-1: Separation Factor of Metals with respect to Calcium for the Carboxylic Resin

Metal Ion	SEPARATION FACTOR	
	pH = 4.1	pH = 6.52
Cd^{2+}	5	190
Cu^{2+}	41	860
Ni^{2+}	2	2
Pb^{2+}	1790	2229
Zn^{2+}	13	38

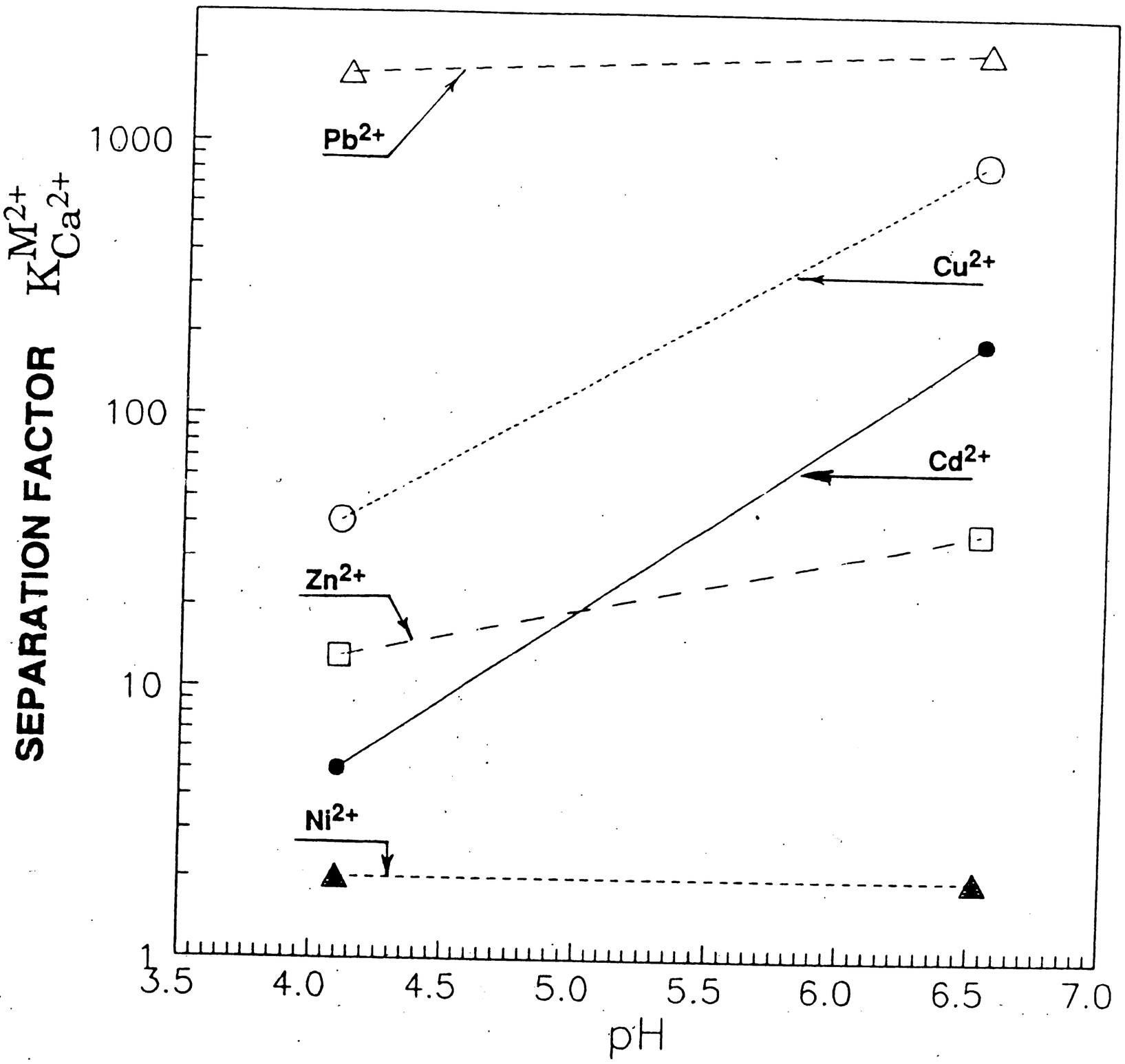


Figure 2-8: Effect of pH on the Metal Ion Selectivity for the Carboxylic Resin

Lead > Copper > Cadmium > Zinc > Nickel

The above selectivity series for the carboxylate resin is in agreement with the selectivity series given by Gindin. It is observed from the column number 2 in Table 2-1 that the separation factor of zinc is more than cadmium ion. Both these two species were present in the resin in microgram level. An analytical error is considered attributable for the reversed order in the separation factor of zinc ion at lower pH i.e. at a pH of 4.1.

2.3.2 Metal Ion Separation Factor with XFS-4195 Resin

The separation factor of different metal ions with respect to calcium for the XFS-4195 resin at a pH of 3.05, 4.15 and 5.15 is plotted in Figure 2-9 and also listed in Table 2-2 to the nearest integer. For the detailed calculations and experimental conditions Appendix C, Appendix D and Appendix E may be referred to. The removal capacity and the metal ion selectivity, except for zinc, of this resin increased with the decrease in aqueous phase pH. In the case of zinc, with this resin, the separation factor improved with the increase in aqueous phase pH. In the case of nickel, the separation factor drops sharply with the increase in pH from 3.05 to 4.15. The capacity of this resin was observed as 0.922 meq/gm, 0.845 meq/gm and 0.693 meq/gm at pH 3.05, 4.15 and 5.15 respectively. This resin exhibits a high selectivity for copper with the lead as the least selective species. The selectivity series of this resin, for the metals studied, are as follows:

Copper > Nickel > Cadmium > Zinc > Lead (at pH 3.05) and

Copper > Cadmium > Nickel > Zinc > Lead (at pH 4.15 and above)

Table 2-2: Separation Factor of Metals with respect to Calcium for XFS-4195 Resin

Description	Separation Factor		
	pH = 3.05	pH = 4.15	pH = 5.15
Cadmium	6661	4972	4653
Copper	50990	22831	19961
Nickel	12054	3526	2747
Lead	526	380	589
Zinc	784	1240	1488

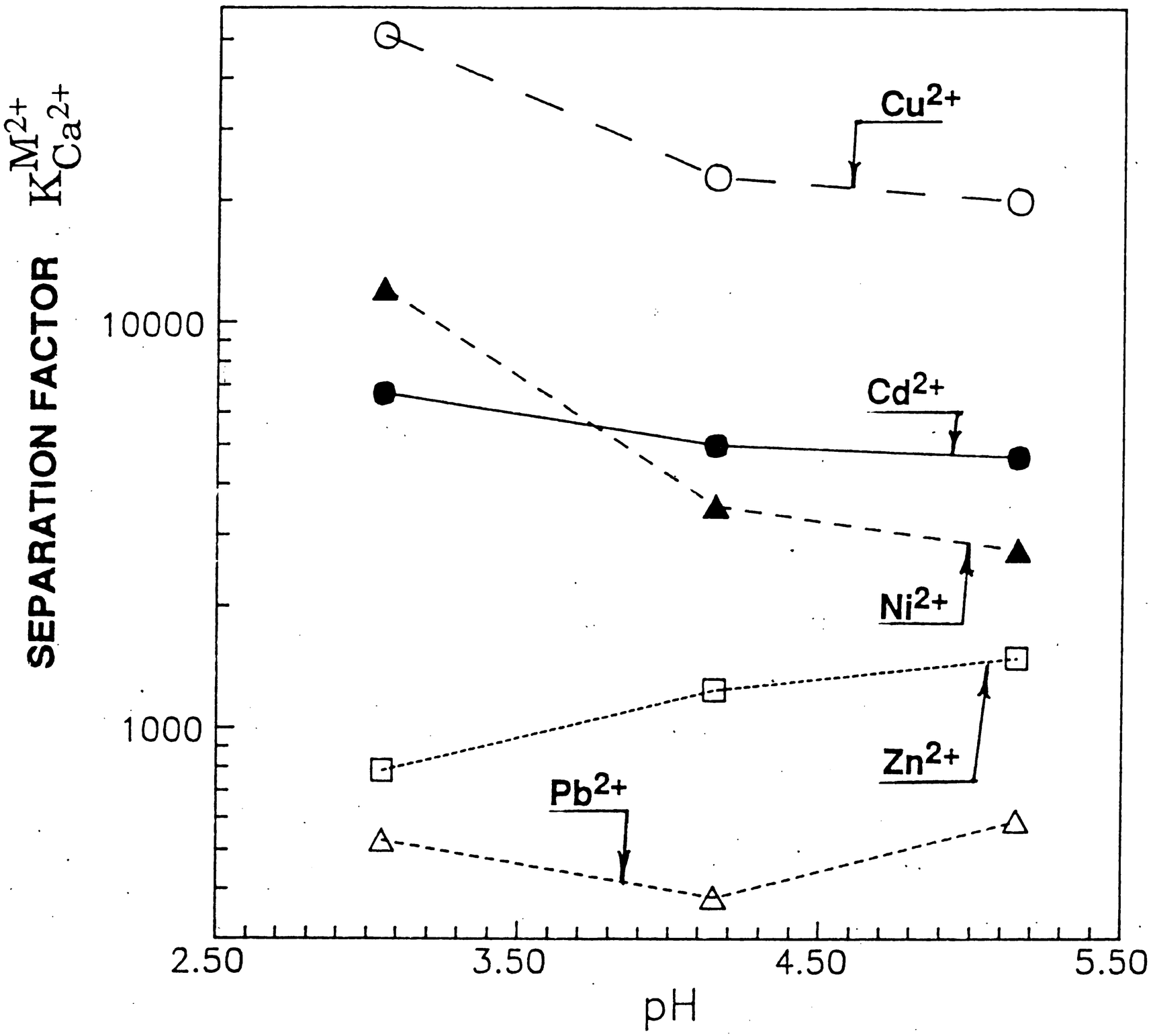


Figure 2-9: Effect of pH on the Metal Ion Selectivity for the XFS-4195 Resin

2.3.3 Metal Ion Separation Factor with GT-73 Resin

The separation factors of the different metal ions with GT-73 resin at a pH of 4.1, 5.15 and 6.52 are plotted in Fig. 2-10. The experimentally determined separation factors are also listed in Table 2-3 to the nearest integer based on the detailed calculations given in Appeindix F, Appendix G and Appendix H. The capacity of this resin at pH 4.1, 5.15 and 6.52 is determined as 1.539 meq/gm, 1.73 meq/gm and 1.662 meq/gm respectively.

Lead is the most selective metal ion for this resin followed by copper. The separation factor for copper and lead increases with the increase in system pH. The separation factor of other metals undergoes little change with a change in the system pH. However, the relative position of cadmium, nickel and zinc changes in the selectivity scale as the system pH is changed. In the order of decreasing separation factors, with GT-73 resin, the individual metals can be ranked as :

Lead > Copper > Zinc > Cadmium > Nickel (at pH = 4.1) ;

Lead > Copper > Nickel > Cadmium, Zinc (at pH = 5.15);

and,

Lead > Copper > Zinc > Nickel > Cadmium (at pH = 6.52)

2.3.4 Metal Ion Separation Factor with IRC-718 Resin

The separation factors of the differnt metal ions with IRC-718 resin at a pH of 4.1, 5.15 and 6.52 are plotted in Fig.2-11. The experimentally determined separation factors are also listed to the nearest integer in Table 2-4 based on the detailed calculations given in Appendix I, Appendix J and Appendix K. The capacity of the resin are determined as 3.129 meq/gm, 3.407 meq/gm and 4.39 meq/gm at a pH of 4.1, 5.15 and 6.52 respectively.

The separation factors of all the metal ions increased with an increase in

Table 2-3: Separation Factor of Metals with respect to Calcium for the GT-73 Resin

Description	Separation Factor		
	pH = 4.1	pH = 5.15	pH = 6.52
Cadmium	3	9	4
Copper	213	534	711
Nickel	2	57	8
Lead	435	870	1190
Zinc	4	8	10

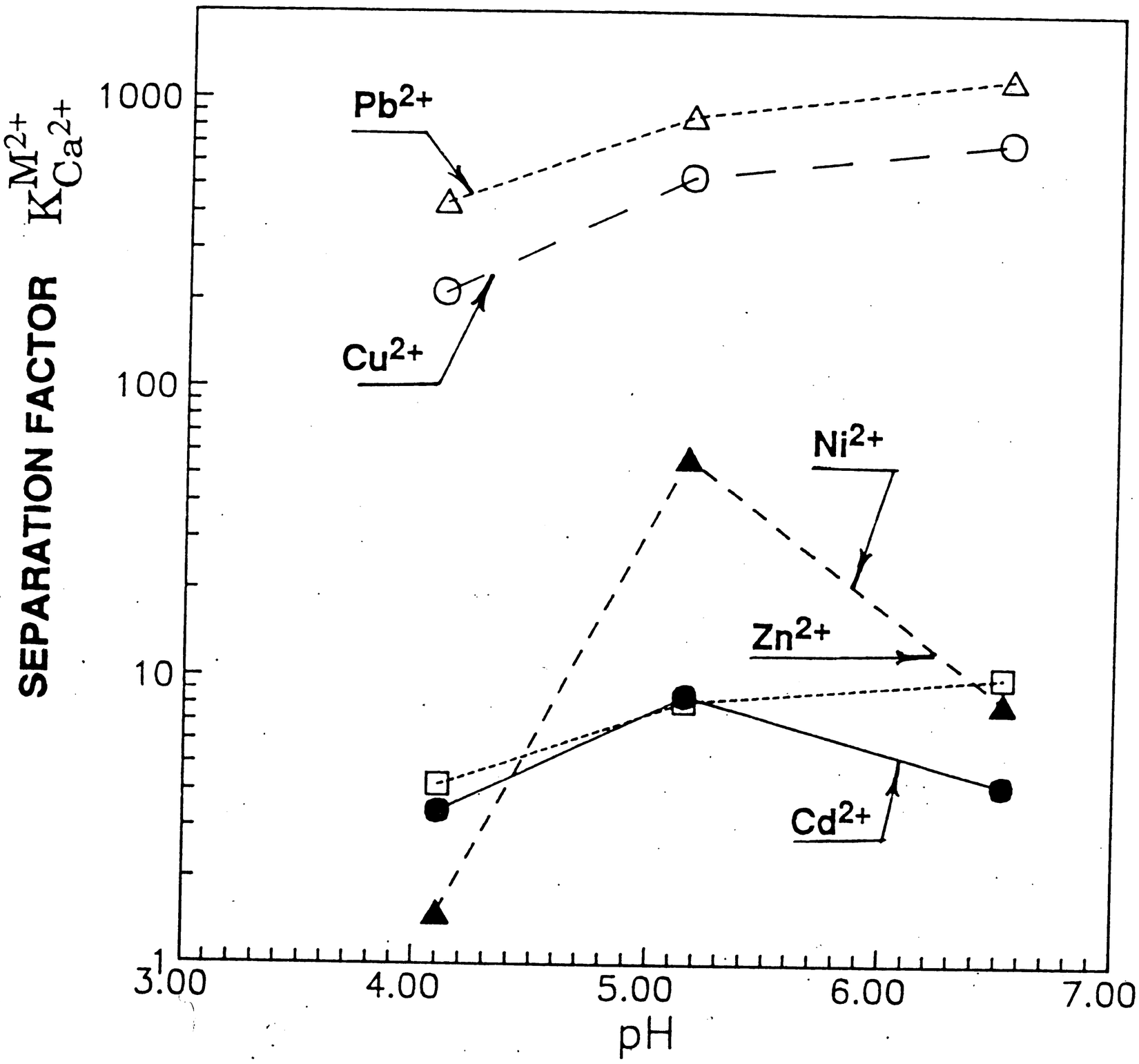


Figure 2-10: Effect of pH on the Metal Ion Separation Factor for the GT-73 Resin

Table 2-4: Separation Factor of Metals with respect to Calcium for the Iminodiacetate Resin

Metal Ion	SEPARATION FACTOR		
	pH = 4.1	pH = 5.15	pH = 6.52
Cd^{2+}	92	518	941
Cu^{2+}	3589	5680	3369
Ni^{2+}	1206	2267	1802
Pb^{2+}	2492	4382	3533
Zn^{2+}	203	884	1361

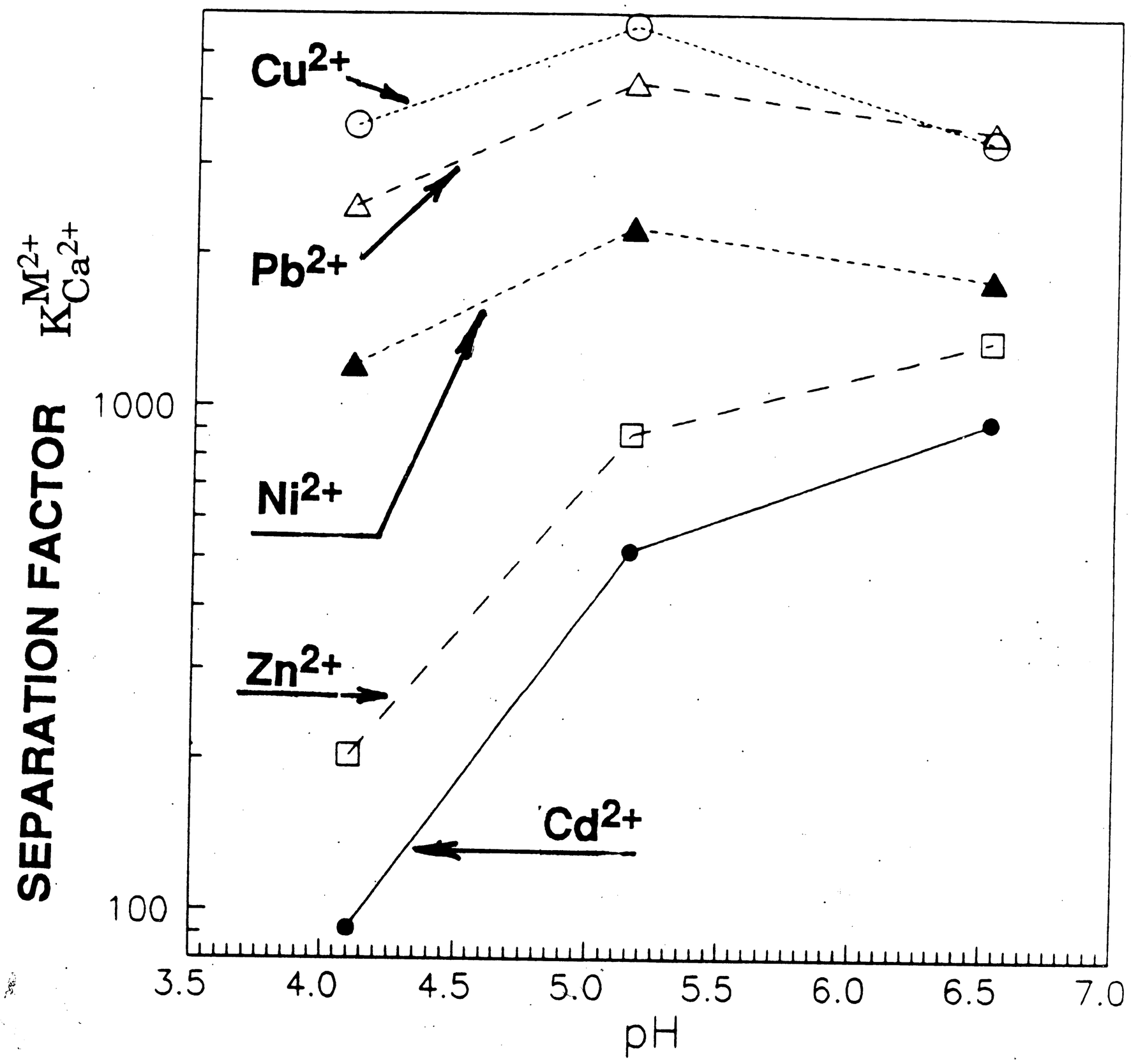


Figure 2-11: Effect of pH on the Metal ion Separation Factor for the Iminodiacetate Resin

pH from 4.1 to 5.15. A further increase in pH from 5.15 to 6.52, resulted in a decrease in the separation factors in the case of copper, nickel and lead ions. However, the separation factors of the cadmium and zinc ion further improved with the increase in equilibrium pH.

Although, all the metal ions had undergone changes in the separation factor, the relative position of the metal ions in the separation factor scale remains unaltered upto a pH of 5.15. It is observed from Table 2-4 that, with the iminodiacetate resin, copper ion is the most preferred species and the cadmium ion is the least preferred species upto a pH of 5.15. At pH 6.52, lead ion has replaced the copper ion to take the top position in the selectivity scale. However, except this interchange in position of lead and copper ion at pH 6.52, the relative position of all other metal ions remains unaltered. In the order of decresing separation factors the individual metal ions can be ranked as :

Copper > Lead > Nickel > Zinc > Cadmium (upto pH = 5.15)

and

Lead > Copper > Nickel > Zinc > Cadmium (at pH = 6.52)

2.4 OBSERVATIONS

Significant findings from the experimental data for the separation factors of the four chelating ion exchange resins with the five metal ions are :

- The application of ion exchange resin with different functionalities depends on the ultimate objective of recovery. The order of selectivity of the metal ions can be changed by changing the

functionality of the resin. As an illustration, if an effluent contains a mixture of lead and copper, carboxylate resin or resin with thiol functional group will prove to be more useful if the objective is to recover the lead while the application of iminodiacetate resin or a resin with nitrogen donor atoms at a low pH will be more effective if the objective is to recover the copper.

- Except for copper, nickel and lead, in the case of iminodiacetate resin at pH 6.52 and in the case of nickel with carboxylic resin, the separation factors of all the metal ions increased with an increase in pH for these two resins. In the case of XFS-4195, the separation factor of zinc increased with pH; and the separation factors for the other metal ions decreased with pH. At pH 5.15, a reversal in selectivity is observed between nickel and cadmium; the more selective species, nickel at pH 3.05, becomes less selective with respect to cadmium at pH 4.15. In the case of GT-73, the separation factor for lead and copper increases significantly with the increase in aqueous phase pH. The pH has little effect on the separation factors of cadmium, nickel and zinc. Thus, with the same ion exchange resin, having a definite functional group, the separation factor of any metal ion can be increased or decreased by changing the system pH to meet the objective of separation or recovery.

- pH can be used as a process variable to optimise the objective of metal recovery from a waste stream. As an illustration, if cadmium is to be recovered from an effluent containing cadmium and zinc using carboxylic resin, use of high pH will result in a better separation between them due to higher cadmium-zinc separation factor at higher pH. On the other hand, if lead is to be recovered from a mixture of lead and copper bearing effluent using carboxylic resin, operation at lower pH will be more effective due to higher lead-copper separation factor at lower pH. Thus pH can be used as a tool to meet the final goal of recovery of metals.

Chapter 3
STUDIES FOR THE METAL BINDING MECHANISM OF THE CHELATING CATION RESINS

3.1 THE METHOD

From the previous chapter it is observed that both the chelating cation resins exhibit an increase in metal selectivity with the increse in the pH of the system with which they are in equilibrium. To explain this phenomenon of the chelating resins studies are madé to find out the binding mechanism of the resins for the metal ions. Scatchard method [49] adopted to analyse the experimental data to find out the possible metal binding mechanism of the resins under different pH conditions. However, for analysing the lead binding mechanism by the carboxylate resin, necessary ^{13}C NMR spectrum of carboxylate resins is taken. The basic features of the Scatchard method for analysing the experimental data to find out the binding mechanism is first discussed in detail.

3.1.1 The Theoretical Aspects of Scatchard Method :Binding by a set of Equivalent and Independent groups

It is considered that the resin molecule R has n groups capable of attaching a metal M. Assuming ideal condition, it permits to set the activities of all the components equal to their concentrations. Considering a special case when n=1, such that MR, the average number of moles of M bound by one molecule of R varies only between 0 and 1, the following reaction can be written.

$$R + M = MR \tag{3.1}$$

If k is the intrinsic binding constant (an association constant) for the above reaction, then

$$k = \frac{[MR]}{[M][R]} \tag{3.2}$$

The average number of moles of M bound per mole of resin can be given by

$$v_i = \frac{k[M]}{1+k[M]} \tag{3.3}$$

Summing for all the number of binding sites (n) present in the resin macromolecule, $v = \sum_{i=1}^{n} v_i = nv_i$ is the total average moles of bound M per mole of R. Therefore,

$$v = \frac{nk[M]}{1+k[M]} \tag{3.4}$$

In Eq. (3.4) above M is the molar concentration of non-bound metal ion i.e. the aqueous phase free metal ion concentration. Equation (3.4) is applicable for a single site or single class of sites with the same intrinsic binding constants. For the evaluation of the parameters of this equation the linear transformation of Eq. (3.4), as proposed by Scatchard, is as follows:

$$\frac{v}{[M]} = kn - kv \tag{3.5}$$

The graphical equivalents of the parameters of Eq. (3.5) are shown in

Figure 3-1. When there is more than one independent classes of sites in the resin macromolecule, the functions given by Figure 3-1 will no longer be a linear one. With m classes of independent sites, each class i, having n_i sites with intrinsic binding constant k_i, the generalised form of Eq. (3.4) can be rewritten as,

$$\frac{v}{[M]} = \sum_{i=1}^{m} \frac{n_i.k_i}{1+k_i[M]} \tag{3.6}$$

The total number of binding sites in the resin, n_0, can be given as,

$$n_0 = \sum_{i=1}^{m} n_i \tag{3.7}$$

Equations (3.4) and (3.6) do not take into account of interactions of any sort between the sites. When there are two or more independent classes of sites, the graphical representation of the Scatchard plot will be as shown in Figure 3-2. The upper part of the curve is due to the strong binding sites present in the macromolecule and the lower part of the curve (near abscissa) is due to the presence of weaker binding sites. From Fig. 3-2 and Eq. (3.6) it is observed that $\frac{v}{M}$ approaches an upper limit of $\sum_{i=1}^{m} n_i k_i$ as v approaches zero, which occurs when m approaches zero. On the other hand, when $\frac{v}{M}$ approaches zero which occurs as M approaches infinity (at a large aqueous phase free metal concentration), v approaches a limiting value of $n = \sum_{i=1}^{m} n_i$.

For a macromolecule with multiple classes of independent binding sites Koltz and Hunston have illustrated [29] that the Scatchard plot, as given by Figure 3-2, can be related to the various parameters as follows.

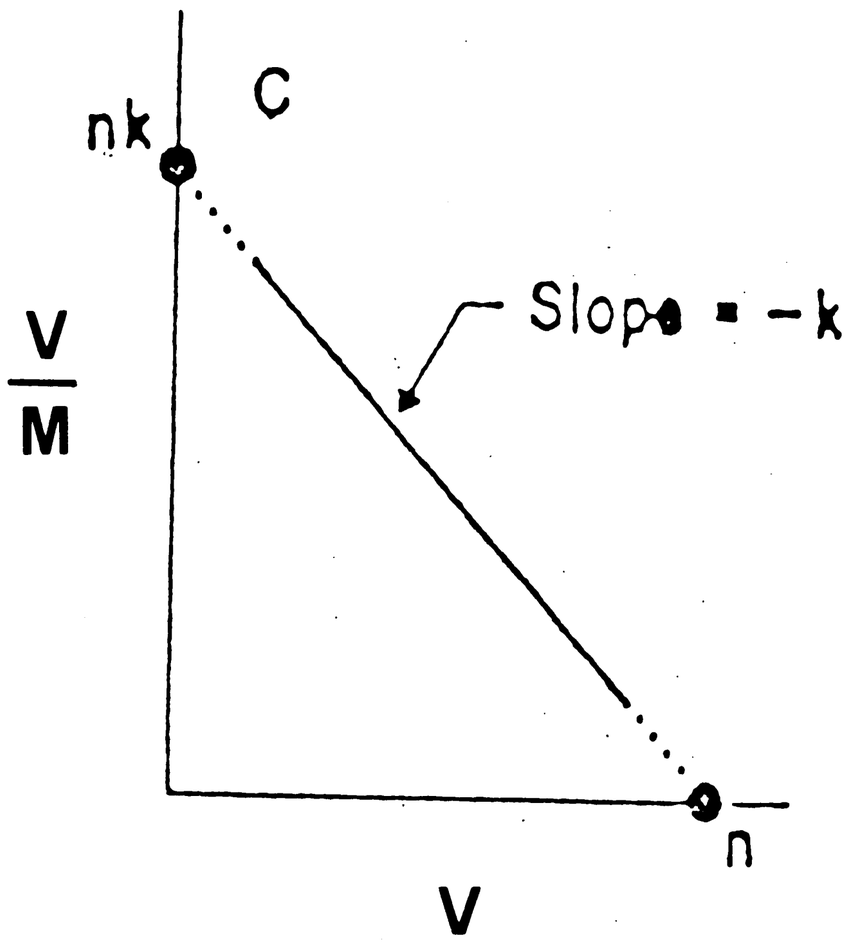


Figure 3-1: Graphical Representation of Scatchard Plot with one binding class

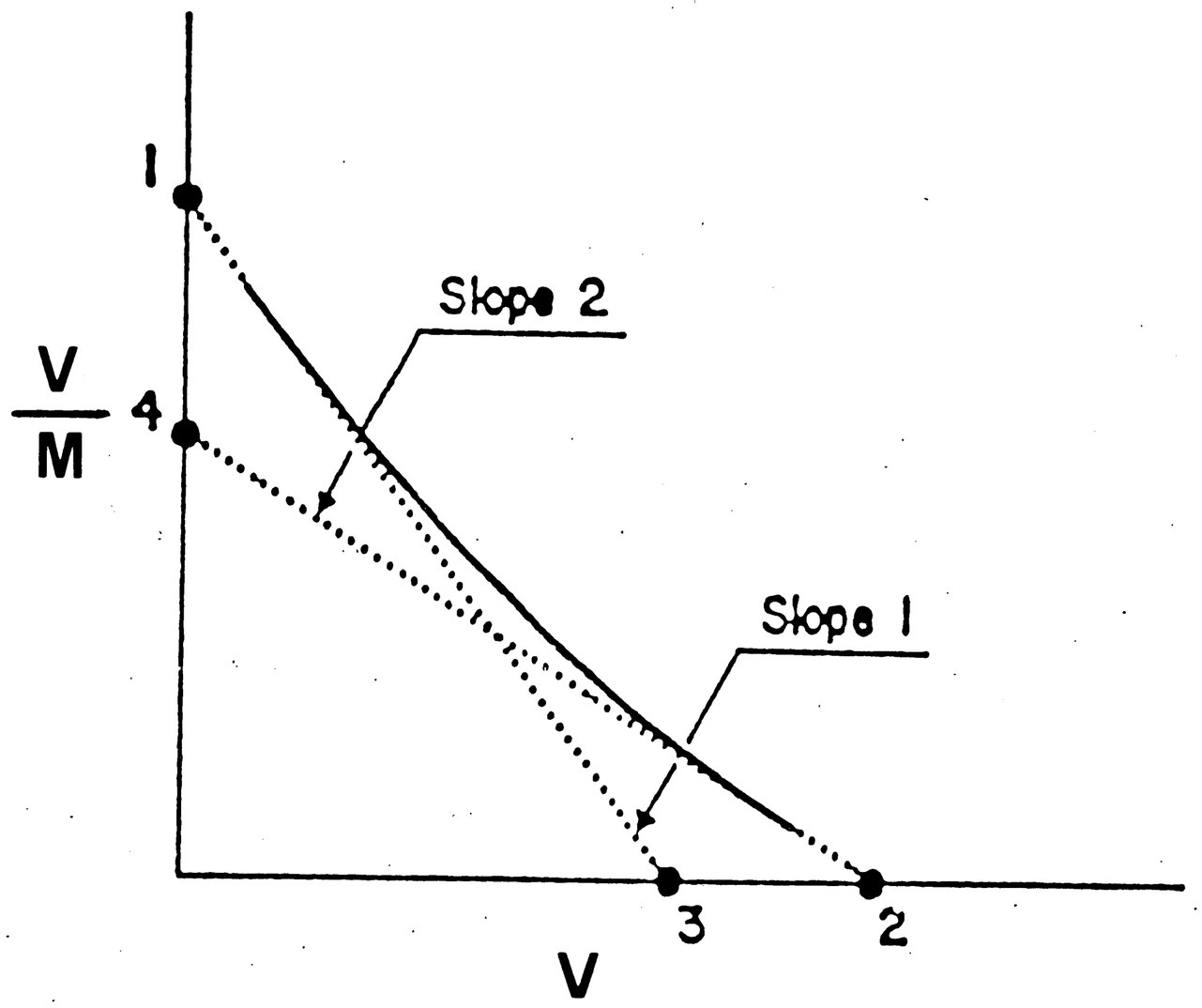


Figure 3-2: Scatchard Plot with Multiple Binding Class

$$\text{Intercept } 1 = \sum_{i=1}^{m} n_i k_i \tag{3.8}$$

$$\text{Intercept } 2 = \sum_{i=1}^{m} n_i \tag{3.9}$$

$$\text{Slope } 1 = \frac{-\sum_{i=1}^{m} n_i k_i^2}{\sum_{i=1}^{m} n_i k_i} \tag{3.10}$$

$$\text{Slope } 2 = \frac{-\sum_{i=1}^{m} n_i}{\sum_{i=1}^{m} n_i / k_i} \tag{3.11}$$

Based on the Equations (3.8) to (3.11), Figure 3-3 shows the parameters for a system with two independent sites with $n_1 = n_2 = 1$. Thus the slopes and intercepts of a Scatchard plot represent various combinations of the intrinsic site binding constants (k_i) and number of binding sites in each class (n_i). Due to the markedly nonlinear nature of Eq. (3.6) and consequently the Scatchard plot, accurate determination of the intercepts in the abscissa and the ordinate is difficult [15, 17, 34]. However, as indicated by Ruzic [30] the presence of two independent class of sites can by identified by Scatchard plot with some precision.

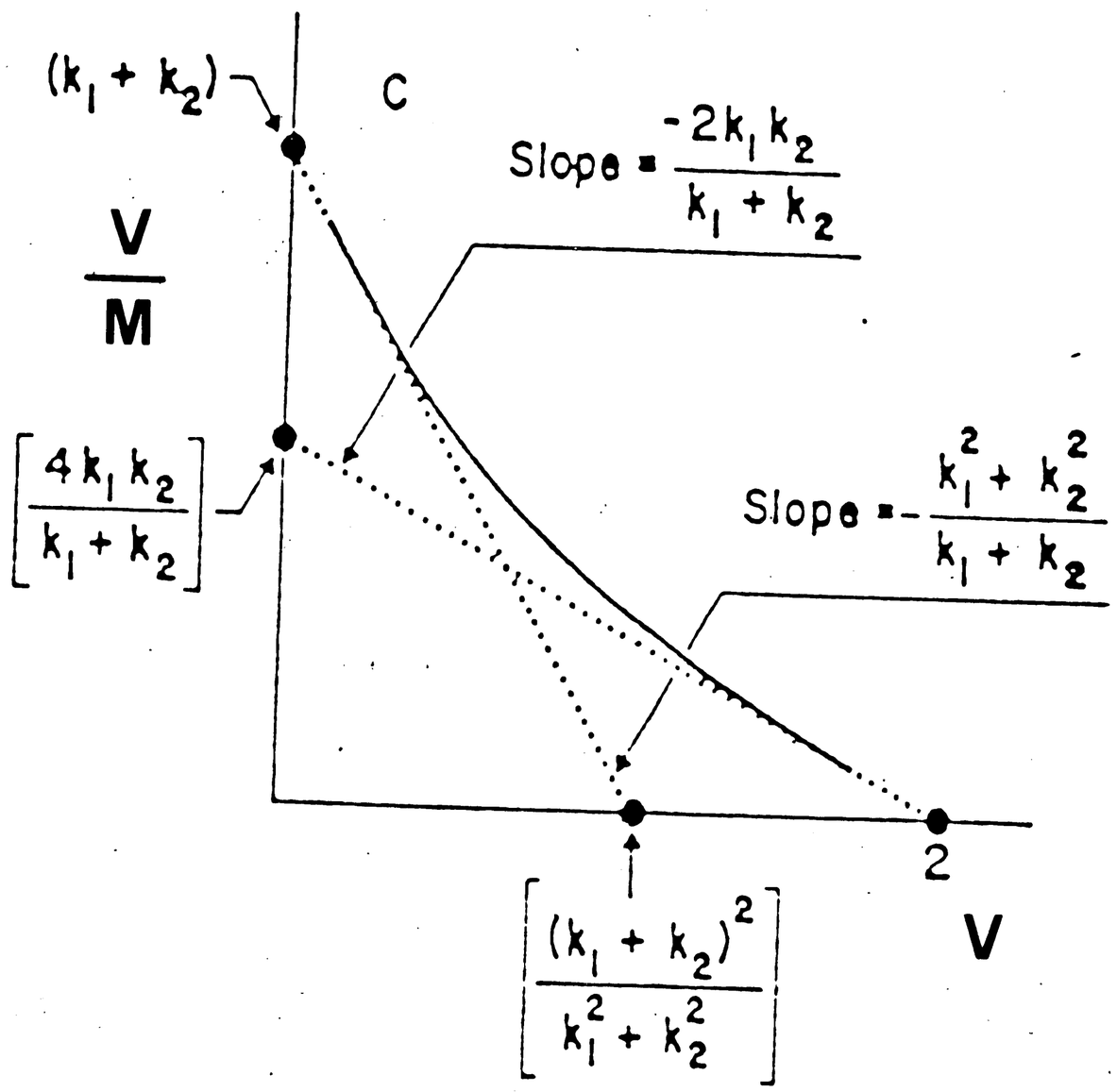
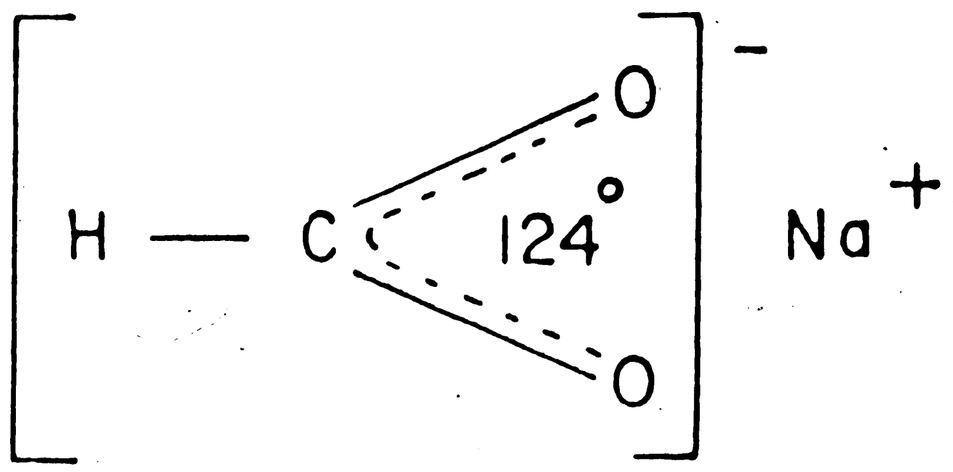


Figure 3-3: Parameters for Scatchard Plot with Two Independent Binding Class

3.2 METAL BINDING MECHANISM OF CARBOXYALTE RESIN

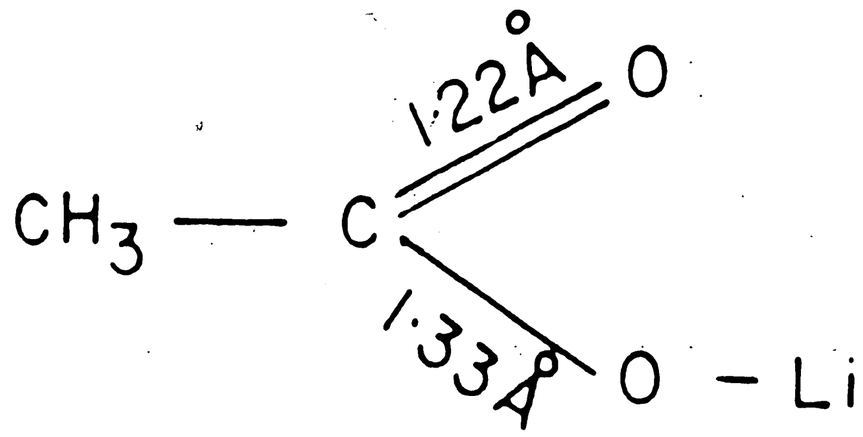
From chemical reasoning Werner [62] had recognised the ability of the acetate groups to bridge two metal atoms in a complex particularly with respect to cobalt. The carboxylate anions ($RCOO^-$) are versatile ligands and capable of binding the metal in (a) ionic (b) unidentate (c) chelating or (d) bridging modes [56, 6]. The interaction between carboxylates and strongly electropositive elements, like sodium and potassium, are reported [63, 5, 53] to be ionic or uncoordinated (ref. Figure 3-4). There seems to be little cation-anion interaction in this mode of metal-carboxylate bonding. In the unidentate chelating mode [19], the metal ion is attached to the carboxylate oxygen atom as RC-O-M (ref. Fig. 3-5). As shown in Figure 3-6, symmetrical and unsymmetrical chelation of metal with both the carboxylate oxygen atoms are observed in the bidentate chelating mode of the carboxylate. Zinc acetate dihydrate $Zn(CH_3COO)_2$, $2H_2O$ is an example [54] of this type of coordination complex of the carboxylates. The bidentate and tridentate coordinating forms [46, 6] of the carboxylate ions are presented in Figure 3-7. The strong coordinated complex forming tendency of the carboxylate ions under this bridging mode leads to the formation of polynuclear metal-carboxylate complexes. Pauling and Sherman observed this type of the bridging mode [50] of the carboxylate ions in the crystal structure of basic berillium acetate $Be_4O(CH_3.COO)_6$.

3.2.1 Binding of Copper by Carboxylate Resin



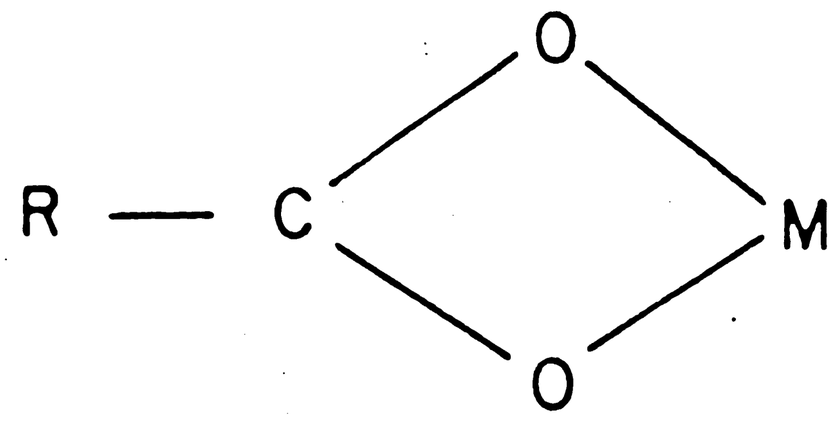
Ionic $Na(O_2CH)$.

Figure 3-4: Un-Coordinated Mode of Carboxylates



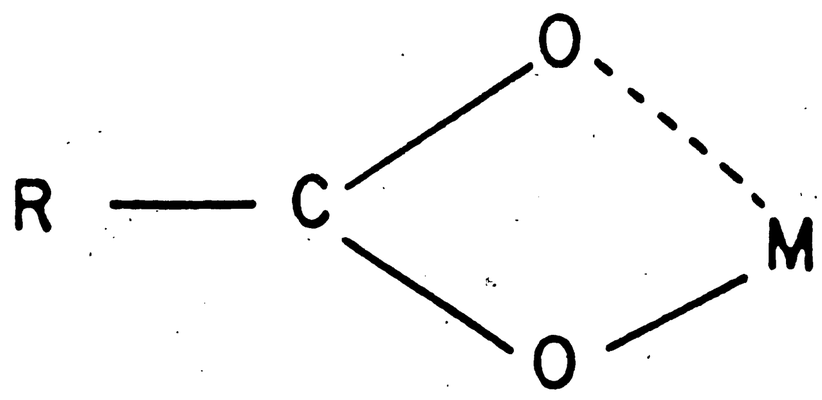
Unidentate $Li(O_2CCH_3)$.

Figure 3-5: Unidentate Mode of Carboxylates



Symmetrical chelating $M(O_2CR)$.

A

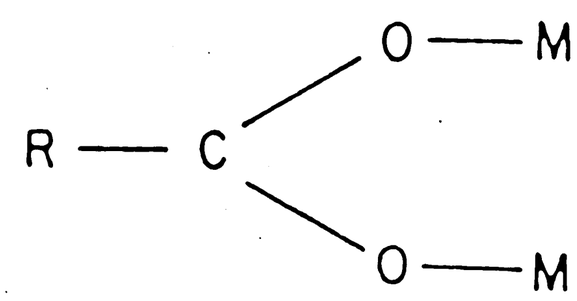


Unsymmetrical chelating $M(O_2CR)$.

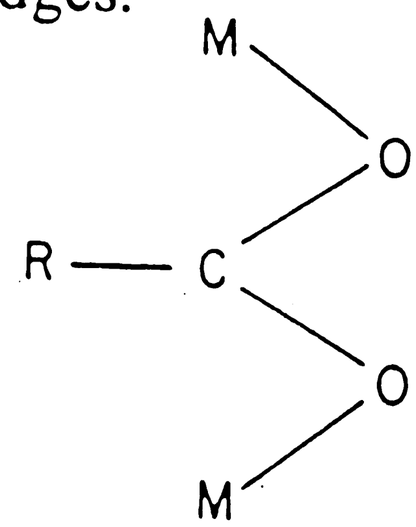
B

Figure 3-6: Symmetrical and Unsymmetrical Bidentate Chelation of Carboxylates

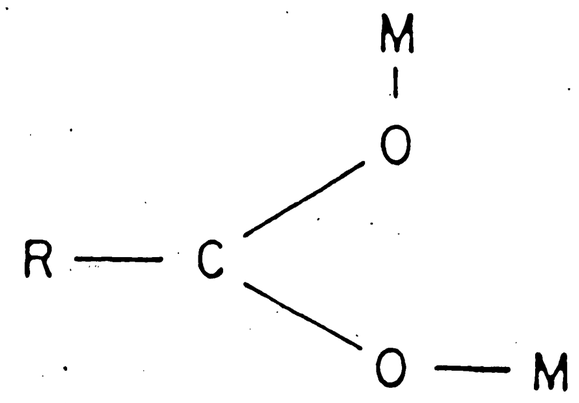
Carboxylate bridges.



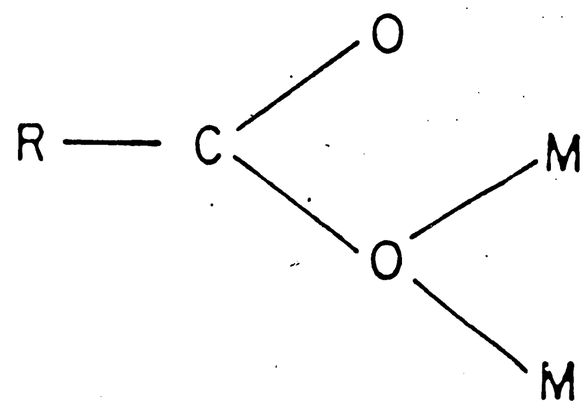
syn – syn



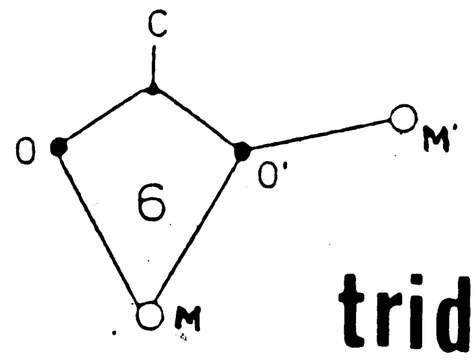
anti – anti



anti – syn



monatomic



tridentate

Figure 3-7: Bidentate and Tridentate Bridging of Carboxylates

3.2.1.1 Review of Contemporary Works

In 1951 Guha [23] studied the temperature dependence (between 83^0K and 304^0K) of the magnetic susceptibility for a number of salts including metal carboxylates. The magnetic susceptibility of crystalline copper(II) acetate monohydrate $Cu(CH_3.COO)_2$, H_2O, instead of obeying the Curie-Weiss law, was found to pass through a maximum near 260^0K and to fall rapidly below this temperature, the extrapolated value being zero near 30^0K. Since then considerable studies have been focused on the nature of neighbouring metal-metal (M-M), metal-oxygen (M-O) and oxygen-oxygen (O-O) interaction in metal carboxylates.

To explain the anomalous magnetic susceptibility data for the cupric acetate monohydrate, experimentally observed by Guha, Bleaney and Bowers [8] in 1952 suggested that isolated pairs of copper(II) atoms interact strongly through exchange forces. However, in the absence of either crystallographic data or isomorphous dilution data, Bleaney and Bowers could not conclude whether direct spin interaction occured between adjacent copper atoms or whether the interaction forces were acting through intermediate oxygen atoms. In 1953 Van Niekerk and Schoening's investigation [59] has shown that copper(II) acetate monohydrate is a binuclear molecule $Cu_2(CH_3.COO)_4$, $2H_2O$, in which the copper atoms are bridged in pairs by four acetate groups with two water molecules occupying the terminal positions (ref. Figure 3-8). The remarkable feature of this sixfold co-ordinated copper(II) complex is the close distance of approach of the two copper atoms of 2.64^0A which is marginally greatrer than the interatomic distance in metallic copper, 2.56^0A. In 1956, Figgis and Martin investigated the temperature dependence of magnetic susceptibility [16] and correlated the antiferromagnetic behaviour to the existence of a δ bond between the adjacent two copper atoms in copper(II)

acetate. Since then, considerable studies, both theoretically and experimentally [9, 24, 37, 40, 25, 7], have been made on this sole dimeric copper(II) acetate complex to explain its antiferromagnetic behaviour. The existence of covalent bonding by the carboxylate oxygen atoms to form a cage like structure, as predicted by Werner in 1910, is evident from Figure 3-8. The crystal structure of polymeric copper-carboxylate complex $[Cu_2(R.COO)_4]_n$ is composed of carboxylato-bridged dimers which are linked into one dimensional polymeric chains (ref. Figure 3-9) by apical Cu-O interactions [46, 31].

With the above background of dimeric and polymeric complexes of copper(II) and carboxylates, the present study addresses the nature of bonding involved between copper(II) and the carboxylate functional groups incorporated in weakly-acidic chelating cation exchange resins. Since ionisation of weakly acidic cation resin is pH dependent, studies for the pH sensitivity on the copper(II) and resin interaction have also been made. Chelating resin with mono-carboxylate functional groups has been evaluated based on the Scatchard method of analysing the experimental data for the titration [49] of resin with copper.

As per the presently belived binding mechanism by carboxylate resin, a bivalent metal is bound to two resin molecules at the RC-OH site oxygen atoms and the protons are released from the exchanging sites to maintain electroneutrality within the system. Under this condition, the nature of the Scatchard plot for the titration of the resin with metal would resemble to Figure 3-1 since only one class of binding site is present into the resin macromolecule. In the contrast, both the oxygen atoms in the resin molecule will independently bind the metal if the resin-metal binding mechanism is identical to that in the copper(II) acetate monohydrate dimer. In the later case, the Scatchard plot for

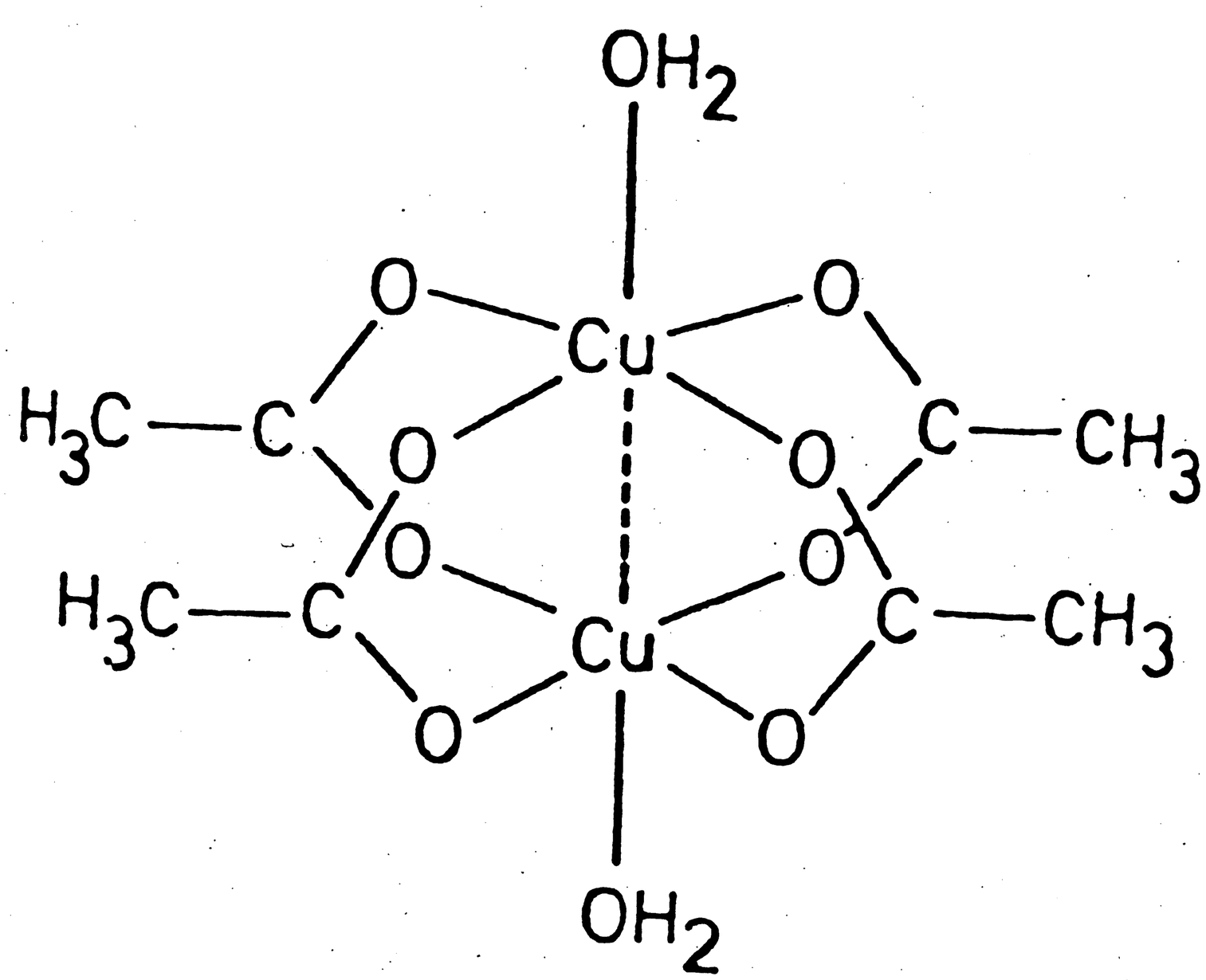


Figure 3-8: Crystal Structure of Copper(II) Acetate Dimer

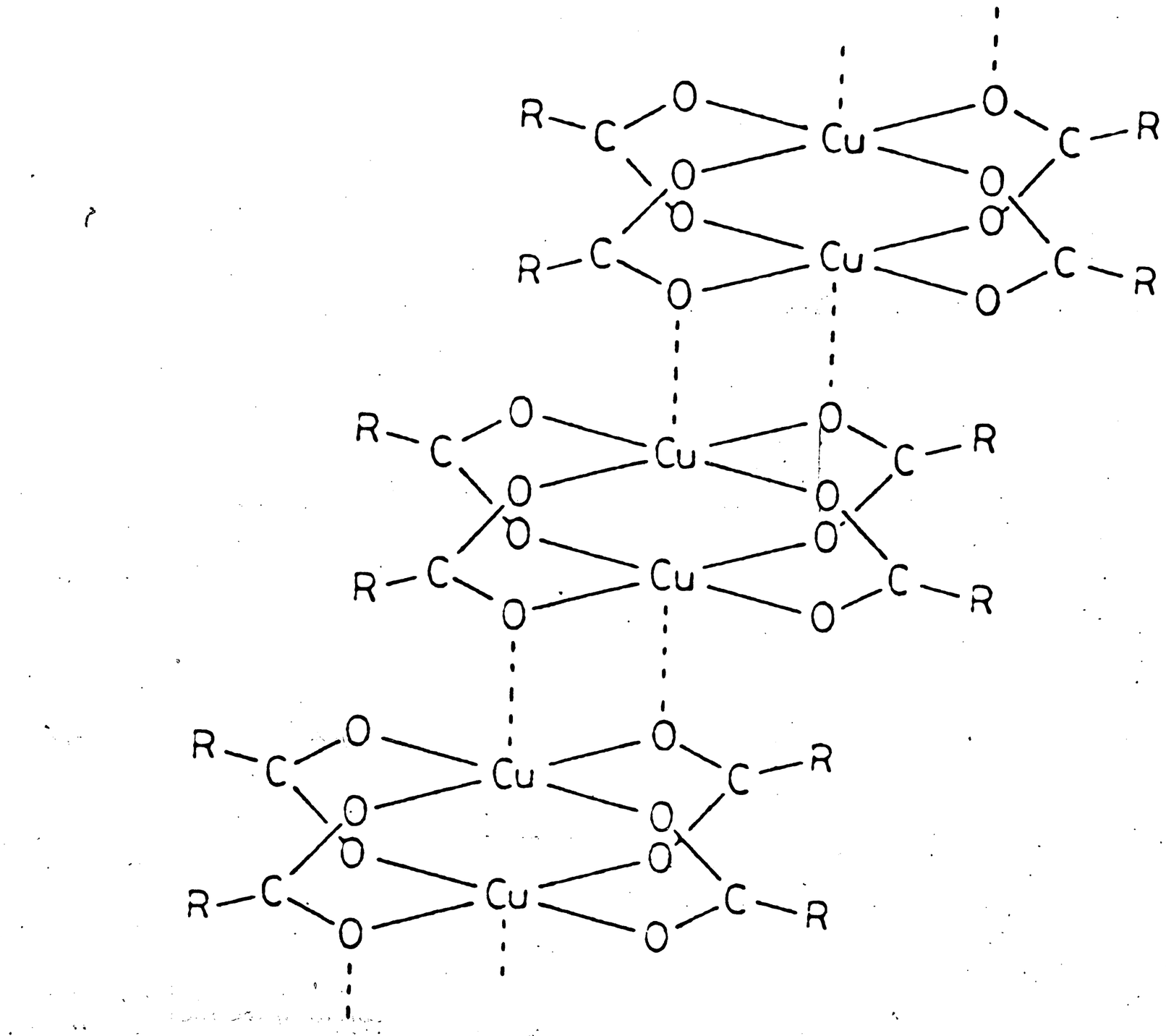


Figure 3-9: Schematic Structure of Polymeric Copper(II) Carboxylates

the resin titration would be analogous to the one shown in Fig. 3-2 and the excess positive charge developed due to covalent bonding with the oxygen atoms, at the C=O site,will be counterbalanced by equal number of negatively charged anions. In other words, the coordinated metal-polymer complexwith covalent bonding to the oxygen atoms, will exhibit anion exchange characteristics in addition to exhibiting the characteristics defined by Fig. 3-2.

3.2.1.2 Experimental

The resin used for the titration is Bio-Rex 70. The average particle size of the resin used in the experiment was between 200-400 mesh. Fine size resin was used to inhibit the kinetic parameters. Four number of resin titration experiment with copper(II) were carried out. In the first and second experiment, henceforth referred as SET1 and SET2 respectively, titration of the resin was carried out at a constant pH of 4.00 + 0.01. Sodium nitrate concentration in SET1 (for experimental data ref. Appendix M) was maintained at 0.048M and the same in SET2 (for experimental data ref. Appendix N) was maintained at 0.11M. In the third and fourth experiment, henceforth referred as SET3 (for experimental data ref. Appendix O) and SET4 (for experimental result ref. Appendix P)respectively, resin titration was carried out at a pH of 5.5 + 0.05. The sodium nitrate concentration in SET3 and SET4 was maintained at 0.048M and 0.11M respectively.

Small amount of wet resin (in sodium form with 70% average moisture content), about 1.6 to 4.0 gm was taken in a 500 ml. beaker with sodium nitrate solution and kept thoroughly agitated. Copper(II) nitrate solution of known concentration, dissolved in the same sodium nitrate solution as that in the main beaker, was added into the beaker until equilibrium attained, as indicated by no change in the system pH, attained within 45-60 minute. To maintain pH of the system, sodium hydroxide, with the same sodium nitrate solution as in the main

beaker, was added. When equilibrium was attained, agitation was stopped and waited till the resin settled. Sample was withdrawn for the analysis of free copper concentration in AA spectrophotometer. A further quantity of copper nitrate was added and agitation repeated. In this way titration curves for the resin were constructed for all the four experiments.

To establish the anion exchange capacity of the resin another four experiments were carried out. In the first and the third experiment, henceforth referred as SSET1 and SSET3 (for experimental results ref. Appendix Q and Appendix R respectively) respectively, vergin resin in sodium form containing 70% moisture was titrated with sodium sulfate at pH 4.00 + 0.01 and 5.5 + 0.05 respectively. In the second and fourth experiment, henceforth referred as SSET2 and SSET4 (for experimental results ref. Appendix S and Appendix T respectively) respectively, copper loaded resin of the experiment SET1 and SET3 respectively, was first filtered using 1.2 um size nylon filter and taken in 500 ml. deionised water followed by titration with sodium sulfate. The pH of SSET2 and SSET4 was maintained at 4.00 + 0.01 and 5.5 + 0.05 respectively. Dilute nitric acid was required to add into all the sulfate titration system to maintain the desired pH. The free sulfate ion concentration was analysed using ion-chromatography.

Computer aided titration meter was used in all the resin titration experiments. The average temperature maintained during the experiments was within $25 + 2^0$C.

SET2 experiment has been basically done to compare certain aspects as discussed later. In Scatchard method of titration one need to to go a high free metal concentration in aqueous phase to attain better interpretation of data. Since in SET2 the aqueous phase copper concentration was only 63 mg/l, which is much less than attained in SET1, SET2 data has not been evaluated for the determination of any parameter.

3.2.1.3 The Result of Resin Titration with Copper(II)

The Scatchard plot with $\frac{v}{M}$ vs. v for SET1 to SET4 experiments is presented from Figure 3-10 to Figure 3-13 respectively. To calculate the v parameter for the Scatchard plot, the chemical structure of the resin as given in Figure 2-1 has been considered [28]. Since the methacrylic acid comprise of the substantial part of the resin structure, the effect of the DVB crosslinking (normally about 6% to 8%) in the molecular wt. of resin has been ignored. For all the Scatchard plots, at very low concentration of free copper(II) in the aqueous phase, a rising trend (distinctly noted in Figure 3-11) in the $\frac{v}{M}$ parameter is observed. After this rising trend the plots are either straight line or curved. No attempt has been made to explain this rising trend of $\frac{v}{M}$ parameter at low copper(II) concentration and kept open for speculation.

From Figure 3-10 and 3-11 it is observed that the Scatchard plots are analogous to Figure 3-1 indicating the presence of only one class of binding site in the resin macromolecule. In the contrast, the nature of the Scatchard plots given by Figure 3-12 and 3-13, for SET3 and SET4 respectively, are analogous to Figure 3-2 indicating the presence of more than one class of binding site in the resin molecule. The parameters of Figure 3-10, Figure 3-12 and Figure 3-13, obtained by linear regression of the data points near the stright line portion of the curves, are summarised in Table 3-1. Based on Eq. (3.8) to Eq. (3.11), the intrinsic binding constants, k_1 and k_2, for the n_1 and n_2 number of binding sites on the resin molecule are obtained from the following equations.

$$k_1 n_1 + k_2 n_2 = \text{Intercept } 1 \tag{3.12}$$

$$n_1 + n_2 = \text{Intercept } 2 \tag{3.13}$$

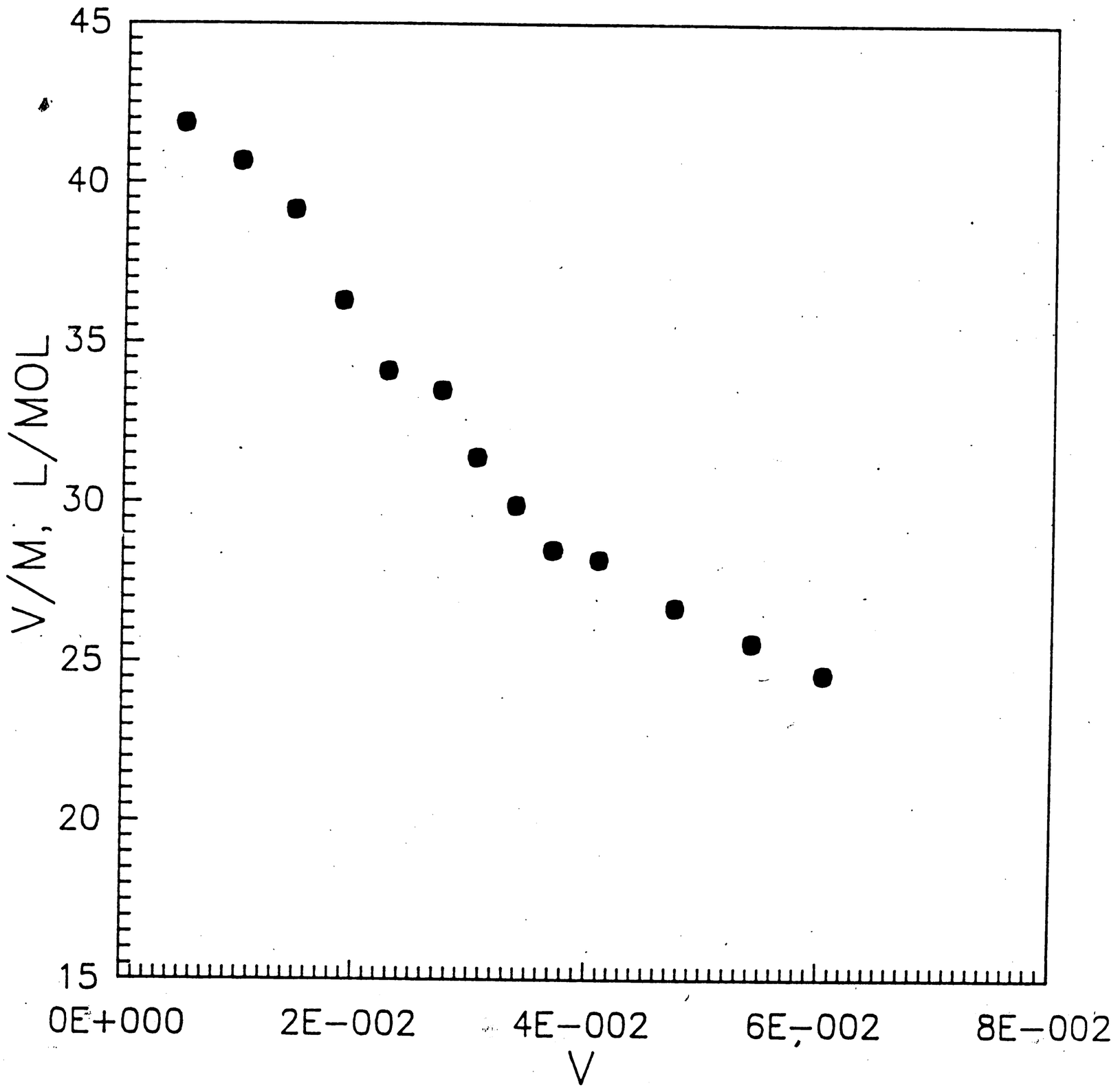


Figure 3-10: Scatchard Plot of Bio-Rex 70 Titration with Copper(II) at pH 4.0 with 0.048M Sodium Nitrate

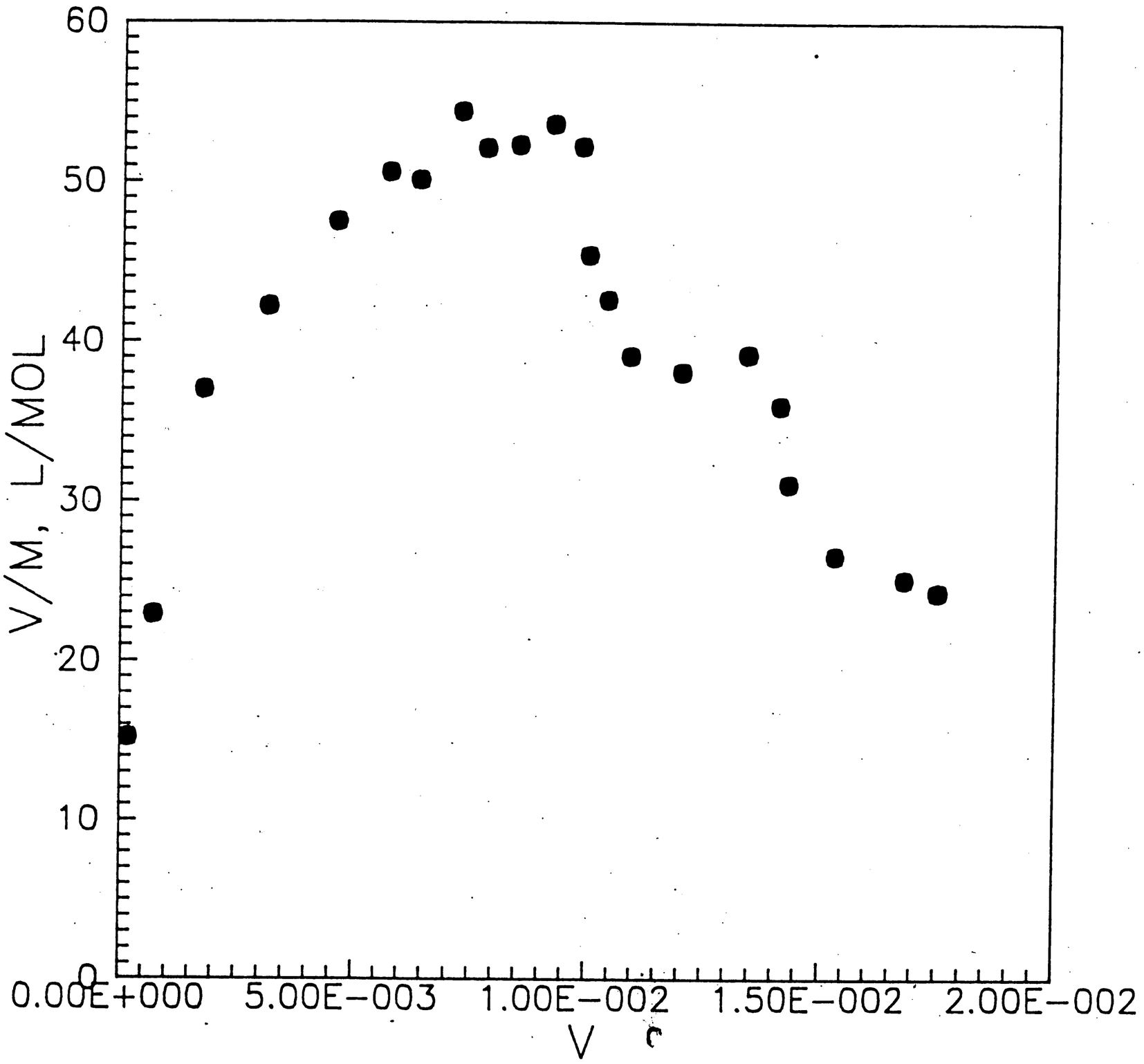


Figure 3-11: Scatchard Plot of Bio-Rex 70 Titration with Copper(II) at pH 4.0 with 0.11M Sodium Nitrate

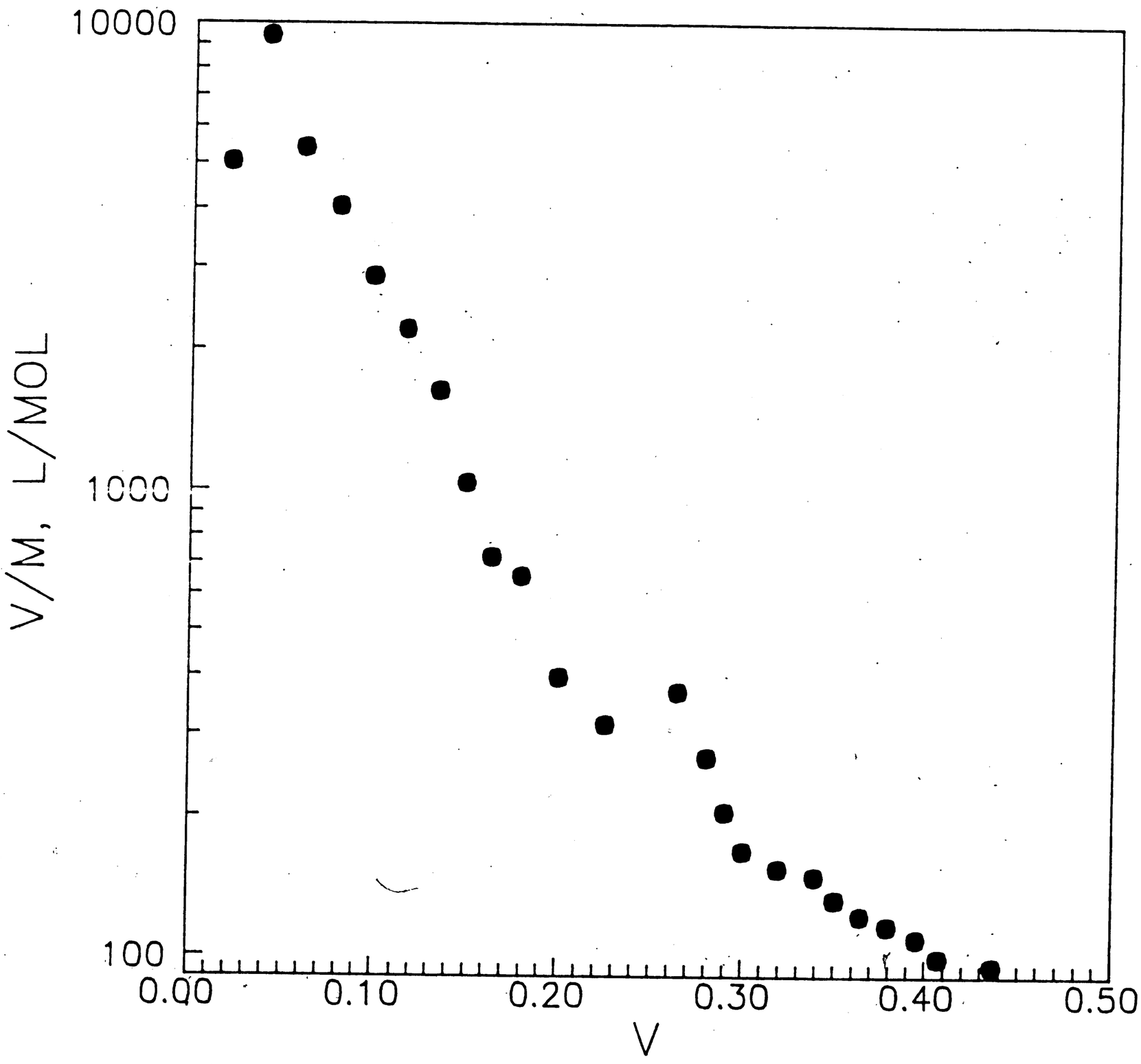


Figure 3-12: Scatchard Plot of Bio-Rex 70 Titration with Copper(II) at pH 5.5 with 0.048M Sodium Nitrate

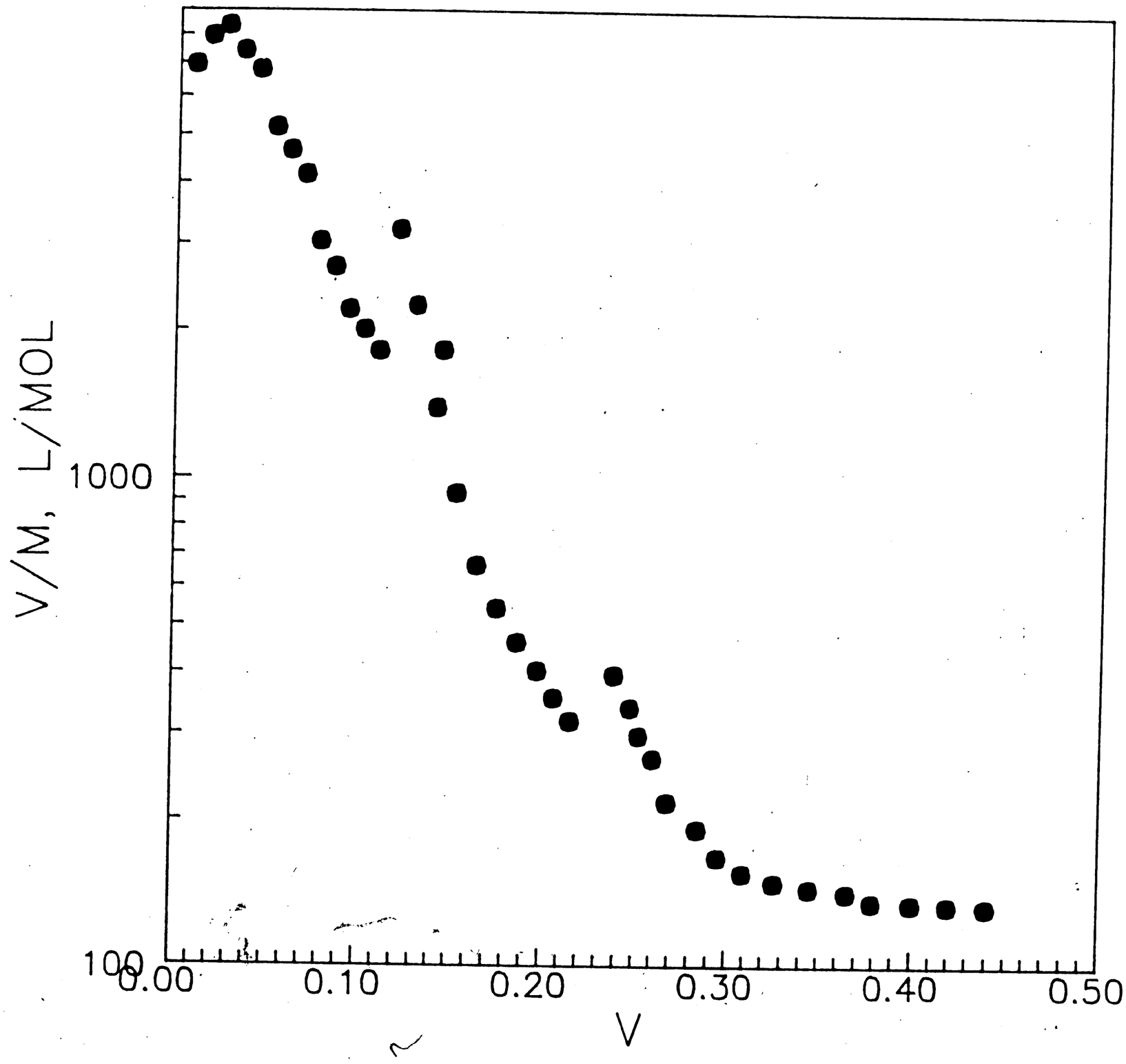


Figure 3-13: Scatchard Plot of Bio-Rex 70 Titration with Copper(II) at pH 5.5 with 0.11M Sodium Nitrate

$$\frac{n_1k_1^2+n_2k_2^2}{n_1k_1+n_2k_2}=\text{Slope}\,1 \tag{3.14}$$

$$\frac{n_1+n_2}{n_1/k_1+n_2/k_2}=\text{Slope}\,2 \tag{3.15}$$

For SET3 AND SET4, the solutions of the Eqs. (3.12) to (3.15) along with the k and n value of SET1 are presented in Table 3-2. At the same sodium nitrate concentration, Table 3-2 shows that the total number of binding sites per mole of resin increases from 0.245 at ph 4.0 to 0.669 at pH 5.5. Again, at pH 5.5 the number of binding sites increases from 0.669 to 1.21 as the sodium nitrate concentration is increased from 0.048M to 0.11M. At a pH of 5.5 the number of binding site of type 1 (n_1) decreases from 0.148 to 0.11 with an increase in sodium nitrate concentration. In the contrast, at the same pH the number of binding site of type 2 (n_2) increases from 0.521 to 1.1 with an increase in sodium nitrate concentration. With an increase in the sodium nitrate concentration, the k_1 of type 1 increases contrary to the decrease in k_2 of type 2 at pH 5.5.

At an equilibrium pH of 5.5, the overall complexation constant for the two step reaction between the resin and copper(II), obtained by multiplying k_1 and k_2, for the SET3 and SET4 is 2.127×10^7 and 1.42×10^7 respectively. Gregor observed [27] the overall complexation constant k_2' to increase from 5.1×10^7 to 8.3×10^5 for a 9% DVB crosslinked resin as the sodium nitrate concentration was increased from 0.0M to 0.2M respectively. Gregor also observed a decrease in the complexation constant with adecrease of the DVB crosslinking in the resin. However, Gregor limited the pH of his titration experiment to 5.0. The present complexation data follows the same trend as observed by Gregor because in both the cases the complexation constant decreases with an increase in sodium nitrate concentration. However from Table 3-2 it is not explicitly clear whether the nature of binding is ion exchange type or covalent or both.

Table 3-1: Graphical Parameters for the SET1, SET3 and SET4 Experiments for the Bio-Rex 70 Titration with Copper(II)

Description	SET1	SET3	SET4
Intercept 1	33.68	10326.9	10417.5
Intercept 2	-	0.669	1.21
Slope 1	-137.29	-67724.7	-90942.0
Slope 2	-	- 396.3	- 169.1

Table 3-2: Intrinsic Binding Constants and Number of Sites of Bio-Rex 70 Titration with Copper(II) for the SET1, SET3 and SET4

Description	SET1	SET3	SET4
n_1	0.245	0.148	0.11
n_2	-	0.521	1.1
k_1	137.29	68793.3	92437.9
k_2	-	309.16	153.6

Since the resin is weakly acidic in nature, it can be considered that the resin is partially ionised at a pH of 5.5. under this condition and in the presence of sodium ions the following two posiible ion exchange reactions between the resin and copper(II) may take place.

$$2RH + Cu^{++} + 2NO_3^- = CuR_2 + 2H^+ + 2NO_3^- \quad (3.16)$$

$$2RNa + Cu^{++} + 2NO_3^- = CuR_2 + 2Na^+ + 2NO_3^- \quad (3.17)$$

Where RH and RNa are the hydrogen and sodium form of the resin respectively. Assuming ideal condition, the stoichiometric equilibrium constant for the above two reactions can be written as:

$$K_{HCu} = \frac{[CuR_2][H^+]^2}{[RH]^2[Cu^{++}]} \quad (3.18)$$

$$K_{NaCu} = \frac{[CuR_2][Na^+]^2}{[RNa]^2[Cu^{++}]} \quad (3.19)$$

Where K_{HCu} and K_{NaCu} are the equilibrium constants for the Eqs. (3.16) and (3.17) respectively. It is apparent from Eq. (3.18) that in a competition reaction between Cu(II) and proton for the same exchange site in resin, at a given hydrogen ion concentration, aqueous phase sodium concentration has no effect on the copper(II) uptake by resin. In the contrast, in a competition between sodium and copper(II) for the same exchange site in resin, Eq. (3.19) shows that the copper(II) uptake by resin will be inversely affected by the aqueous phase sodium concentration. A higher aqueous phase sodium ion concentration will result in lower copper(II) uptake by resin.

The covalent interaction between the resin and copper(II) may be presented by the following equation.

$$RH^{+}.OH^{-}+Cu^{++}+2NO_3^{-}=RCu^{++}.OH^{-}.NO_3^{-}+H^{+}+NO_3^{-} \quad (3.20)$$

Where, $RH^{+}.OH^{-}$ is the proton associated resin molecule with OH^{-} ion to maintain electroneutrality condition and $RCu^{++}.OH^{-}.NO_3^{-}$ is the covalently attached copper(II)-resin complex. Under ideal condition the equilibrium constant for the reaction given by Eq. (3.20) can be written as:

$$K_{RCu}=\frac{[RCu^{++}OH^{-}NO_3^{-}][H^{+}]}{[RH^{+}OH^{-}][Cu^{++}][NO_3^{-}]} \quad (3.21)$$

Where K_{RCu} is the equilibrium constant for the reaction expressed by Eq. (3.20). Equation (3.21) shows that at a given hydrogen ion concentration in the aqueous phase, copper(II) uptake by resin will increase with the aqueous phase anion (consequently total electrolyte) concentration.

Figure 3-14 shows the superimposed plot of the mmol of copper(II) uptake (q) per gm. of resin vs. the aqueous phase copper concentration (C) in mmol/l. for the SET1 and SET2 . The resin phase copper concentration is almost same for both the 0.048M and 0.11M sodium nitrate concentration upto an aqueous phase copper concentration of about 0.3 mmol/l. after which the copper (II) uptake for the system, with low sodium nitrate concentration, is higher than that in the system with higher sodium nitrate concentration. This phenomenon is also predicted from Eqs. (3.18) and (3.19). Hence at pH 4.0 the interaction between copper(II) and resin is essentially ion exchange type and copper(II) is competiting for sites occupied by both the hydrogen and sodium in the resin. As

a verification of this postulation, sulfate uptake by vergin resin and copper loaded resin is presented in Figure 3-15 where the mmol of sulfate uptake per gm (q) of resin is plotted vs. the aqueous phase sulfate concentration (C) in mmol/l. Figure 3-15 shows that the sulfate uptake by the vergin resin (SSET1) is same as that of copper loaded resin (SSET2) upto an aqueous phase sulfate concentration of 2.3 mmol/l. after which the sulfate uptake of SSET1 is higher than SSET2. The lower sulfate uptake by the copper loaded resin at higher aqueous phase sulfate concentration is presumably due to the stearic hindrance from the preoccupied copper in the resin sites.

In Figure 3-16 the superimposed q vs c plot for the copper uptake by resin at pH 5.5 for the SET3 and SET4 is presented. It is observed that irrespective of aqueous phase sodium nitrate concentration the resin phase copper concentration is same upto a free copper concentration of 0.3 mmol/l. For a free copper concentration between 0.3 and 2.2 mmol/l., the copper uptake by resin is higher for the system with lower sodium nitrate concentration. Above 2.2 mmol/l of aqueous phase copper concentration, the copper uptake by resin is higher in the system with higher sodium nitrate concentration. Hence, all the conditions given by Eqs. (3.18), (3.19) and (3.21) are observed to hold good towards explaining the copper uptake by resin at pH 5.5. Hence both covalent and ion exchange type binding mechanism, between the resin molecule and copper(II) are believed to be present at pH 5.5. This binding mechanism is attested by Figure 3-17 where sulfate uptake of SSET3 and SSET4 at pH 5.5 is superimposed and it is observed that the sulfate uptake by the copper loaded resin, at every corresponding aqueous phase sulfate concentration, is about twice than that for the vergin resin with an error of about 8%. Figure 3-17 shows that binding the copper(II) into the resin resulted a development of excess positive charge which is being neutralised by the double charged sulfate ions

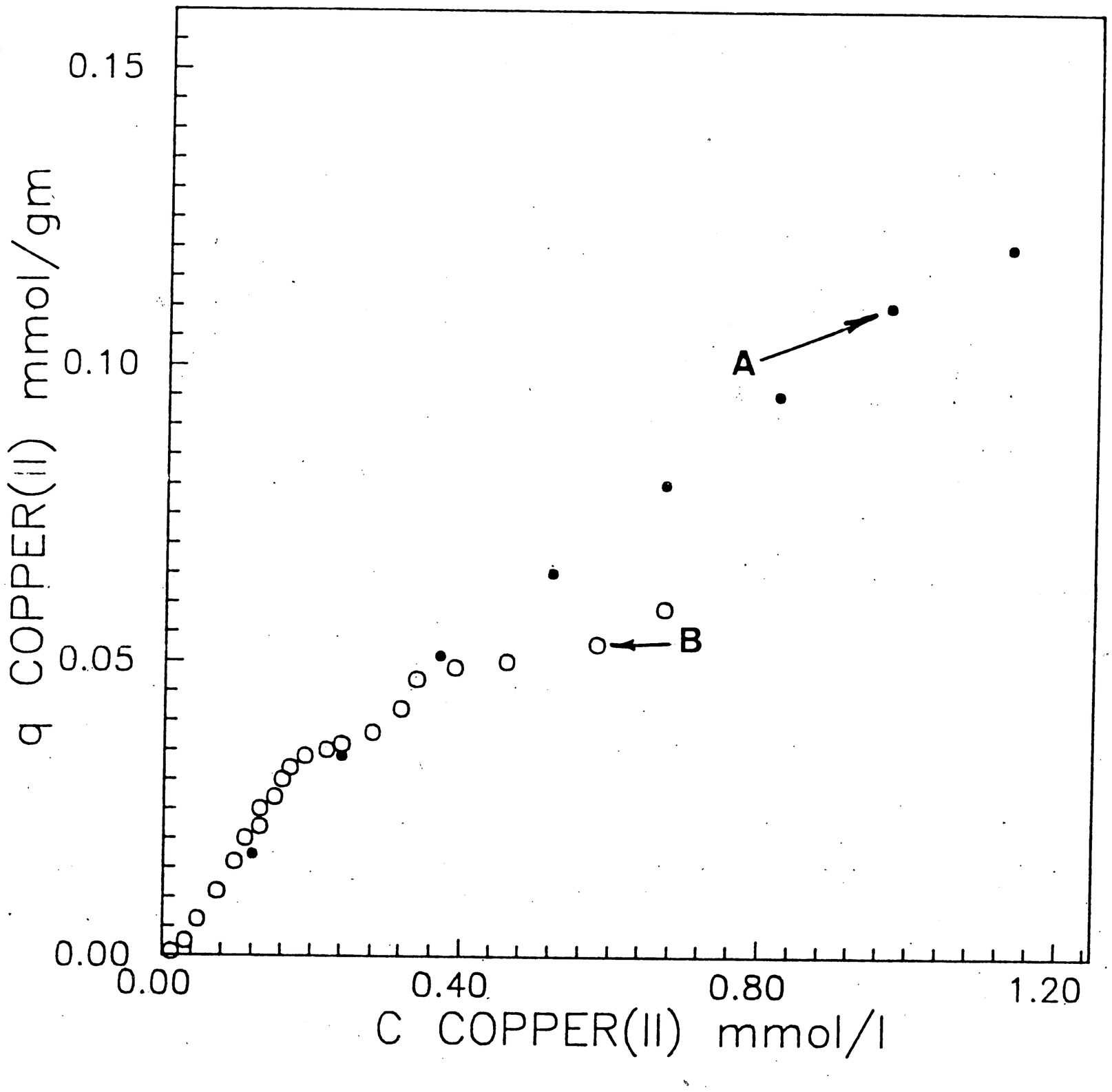


Figure 3-14: Copper(II) Isotherm of Bio-Rex 70 at pH 4.0 (A) 0.048M Sodium Nitrate (B) 0.11M Sodium Nitrate

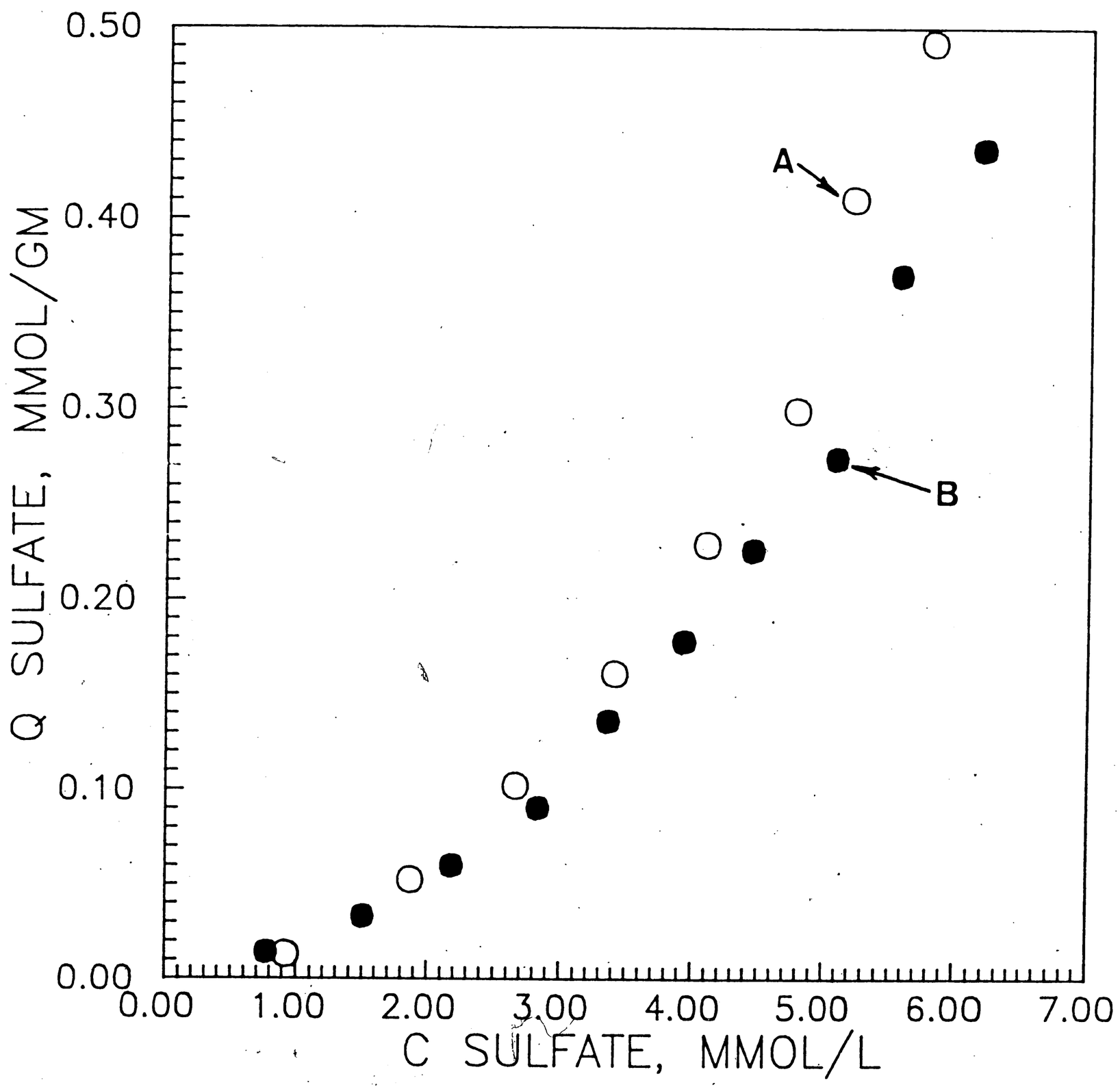


Figure 3-15: Sulfate Uptake by Bio-Rex 70 at pH 4.0 (A) Vergin Resin (Sodium Form) (B) Copper(II) Loaded Resin

displacing some monovalent co-ions. Thus both the oxygen atoms in the carboxylate functional group are independently responsible for binding the copper; the oxygen atom at RC-O-H site is responsible for the ion exchange type interaction between the resin and the copper, and the oxygen atom at RC=O site is responsible for the covalent binding of the copper(II).

An interesting feature of the sulfate titration of resin experiment was that external addition of acid was required to add to maintain the pH of the system. In the chromatogram, a marginal reduction in the aqueous phase nitrate (dilute nitc acid used to maintain pH) was observed. If the proton was associated with a nitrate ion in the resin to maintain electroneutrality condition, during titration with sodium sulfate the nitrate concentration in the aqueous phase should have increased by equivalent amount of sulfate adsorbed by resin. Since both nitrate and sulfate are anions of strong acid, the pH during sulfate titration of resin should also have remained practically constant. In the contrast, acid was added to maintain pH during the resin titration with sodium sulfate. From this phenomenon of resin it may be assumed that possibly some hydrogen bonding exists between the oxygen atoms in the resin molecule.

Referring back to Table 3-2 it can now be identified that n_1 is the number of binding sites for the ion exchange interaction of resin and n_2 is the number of binding sites for the covalent interaction between resin and copper(II). The k_1 and k_2 are the intrinsic binding constant for the ion exchange sites and covalent sites respectively in the carboxylate functional groups.

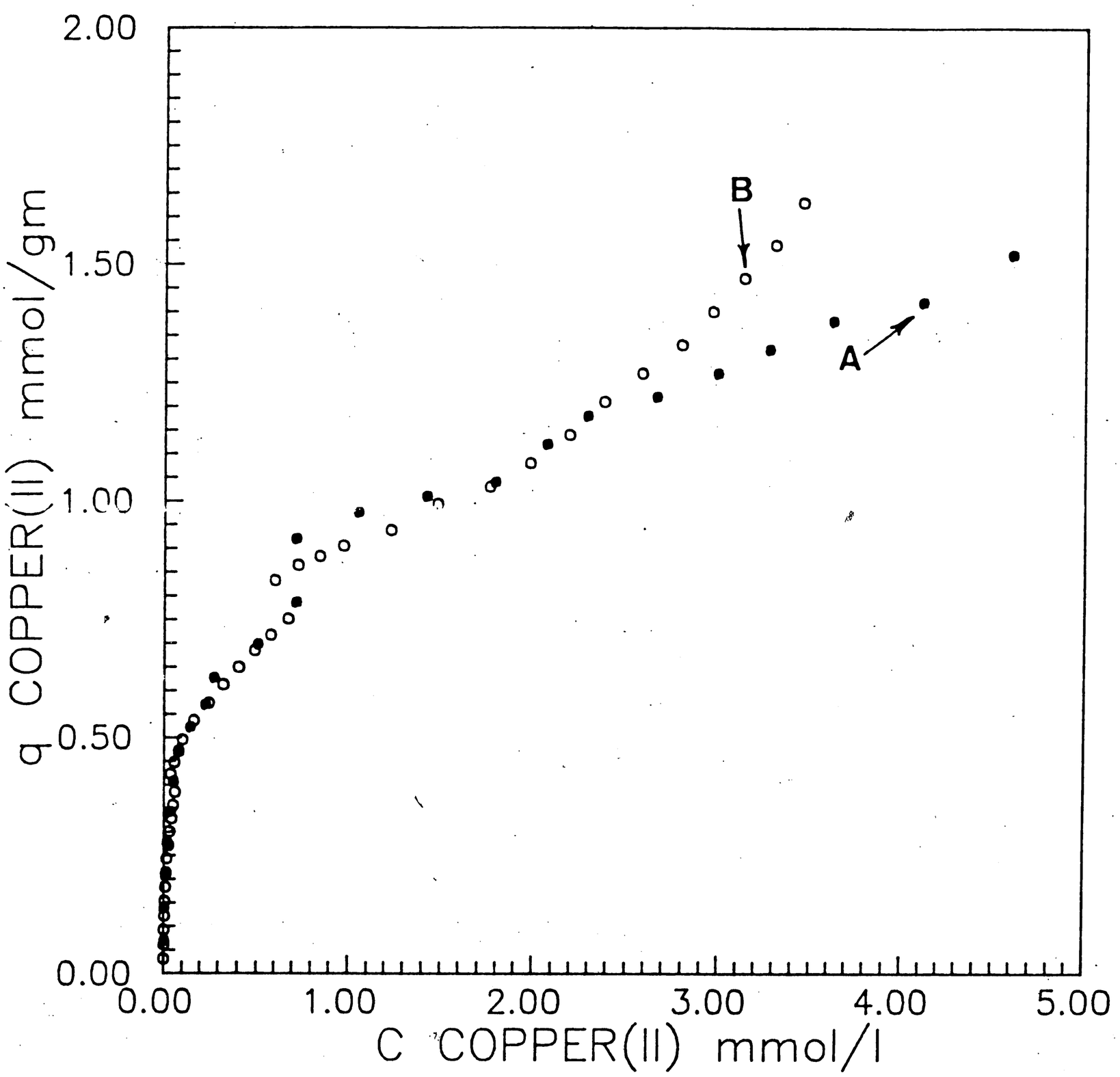


Figure 3-16: Copper(II) Isotherm of Bio-Rex 70 at pH 5.5 (A) 0.048M Sodium Nitrate (B) 0.11M Sodium Nitrate

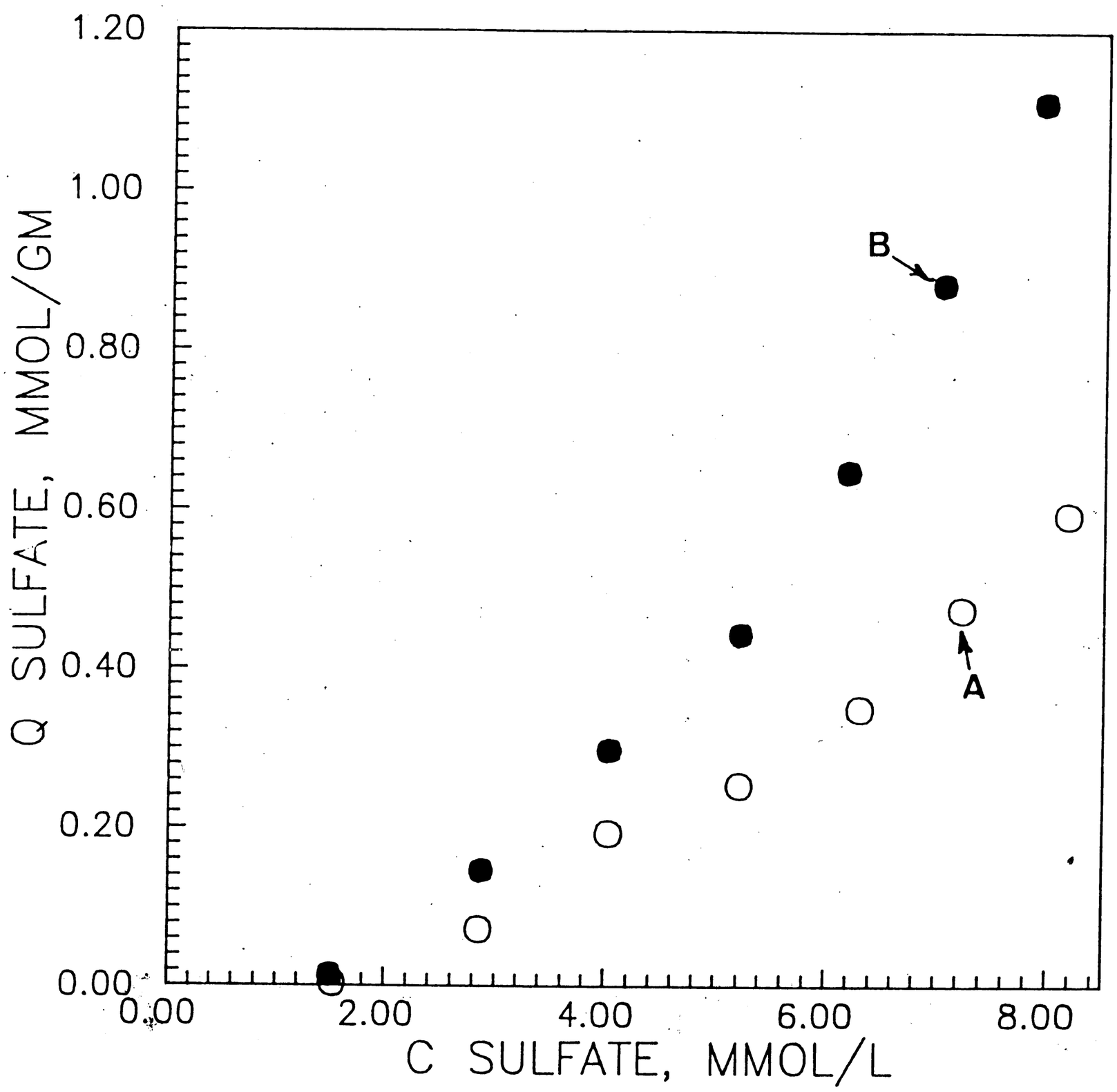


Figure 3-17: Sulfate Uptake of Bio-Rex 70 at pH 5.5 (A) Virgin Resin in Sodium Form (B) Copper Loaded Resin

3.2.2 Binding of Lead by the Carboxylate Resin

Unlike copper, lead carboxylates have been little studied. The IR and ^{1}H NMR data indicate that the bidentate lead acetate has the chemical formula as $Pb(CH_3COO)_4$. Alcock, Tracy and Waddington [57] carried out conductimetric titrations of lead acetates and concluded that the this compound contain bidentate acetate groups with eight-coordinated oxygen atoms.

The ^{13}C NMR spectra for the DP-1 resin in complete Hydrogen form is given in Fig. 3-18 along with the expansion at 10-60 ppm (ref. Fig. 3-19) and 170-190 ppm (ref. Fig. 3-20). The DP-1 resin in Ca form was then equilibrated with a lead solution at pH 5.5 and then air dried. The ^{13}C NMR spectra of this lead loaded resin is given in Figure 3-21 along with its expansions at 10-60 ppm (ref. Fig. 3-22) and 170-190 ppm (ref. Fig. 3-23) chemical shift. This ^{13}C NMR spectrum for the lead loaded resin shows no chemical shift of the carboxylate (at 182 ppm) groups from the parent resin although the resin regeneration data show that 6.8 meq. of lead is present per gm of the resin. The NMR spectrum of the parent resin is consistent with the resin structure with peaks at 18 ppm, 45 ppm, 55 ppm and at 182 ppm of chemical shifts indicating the presence of methyl, ethyl, quatnary carbon and carboxylate groups respectively.

The ^{13}C NMR spectra of DP-1 resin equilibrated with calcium at pH 5.5 is presented in Fig. 3-24 along with its expansions at 10-60 ppm and 170-190 ppm of chemical shifts (ref. Figs. 3-25 and 3-26). From the NMR spectra of the calcium loaded resin has a chemical shift of the carboxylate group at 182 ppm by about 5 ppm. This indicates that the neighbouring oxygen atom in the carboxylate has shifted towards the calcium resulting in a chemical shift. In the contrast, the stability of the carboxylate chemical shifts in the lead loaded resin can only be explained by the fact that both the oxygen atoms in the carboxylate group were attracted by the lead to an equal extent and thus the resultant chemical shift is zero from the parent resin.

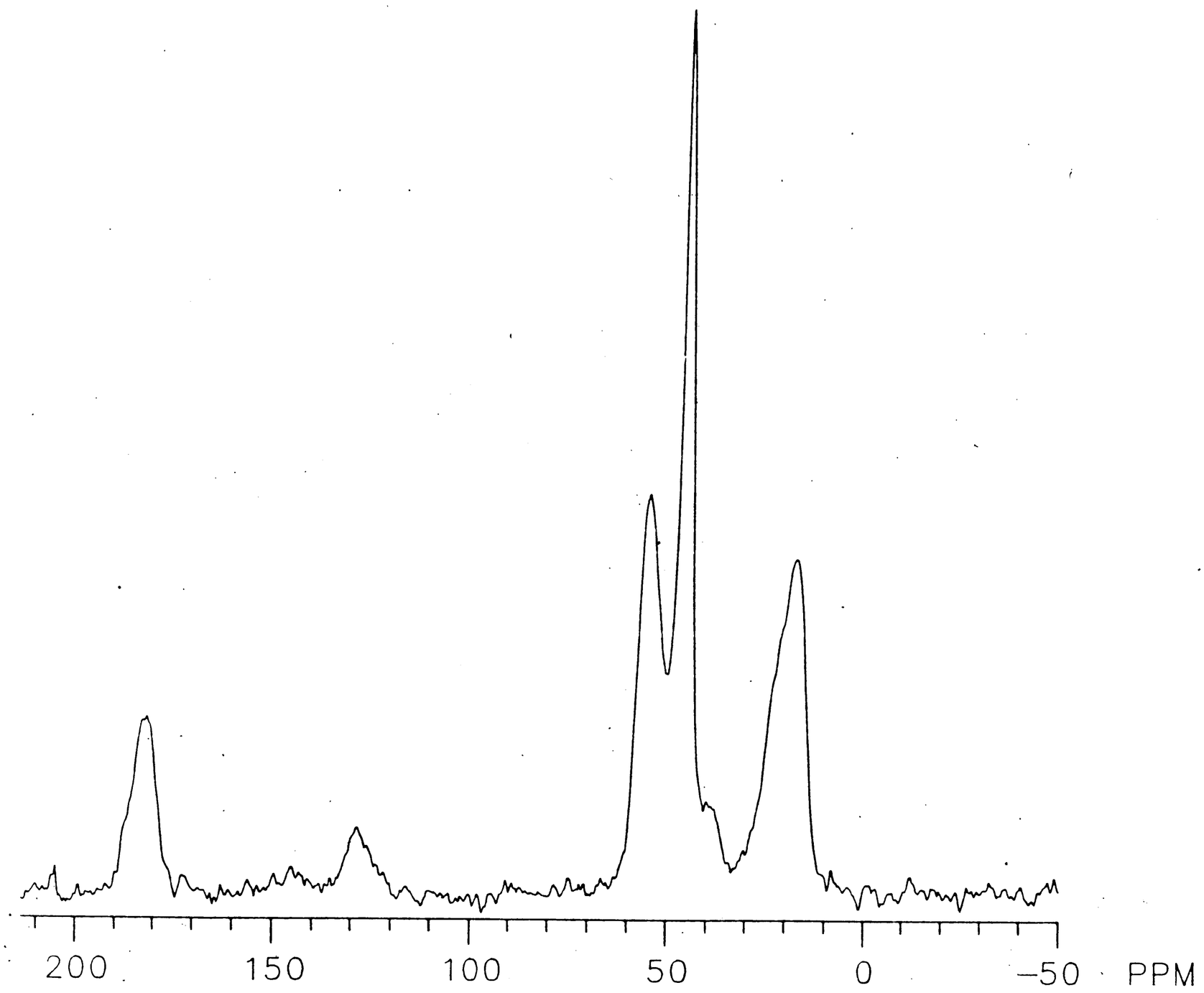


Figure 3-18: ^{13}C NMR Spectra of DP-1 Resin in Hydrogen Form

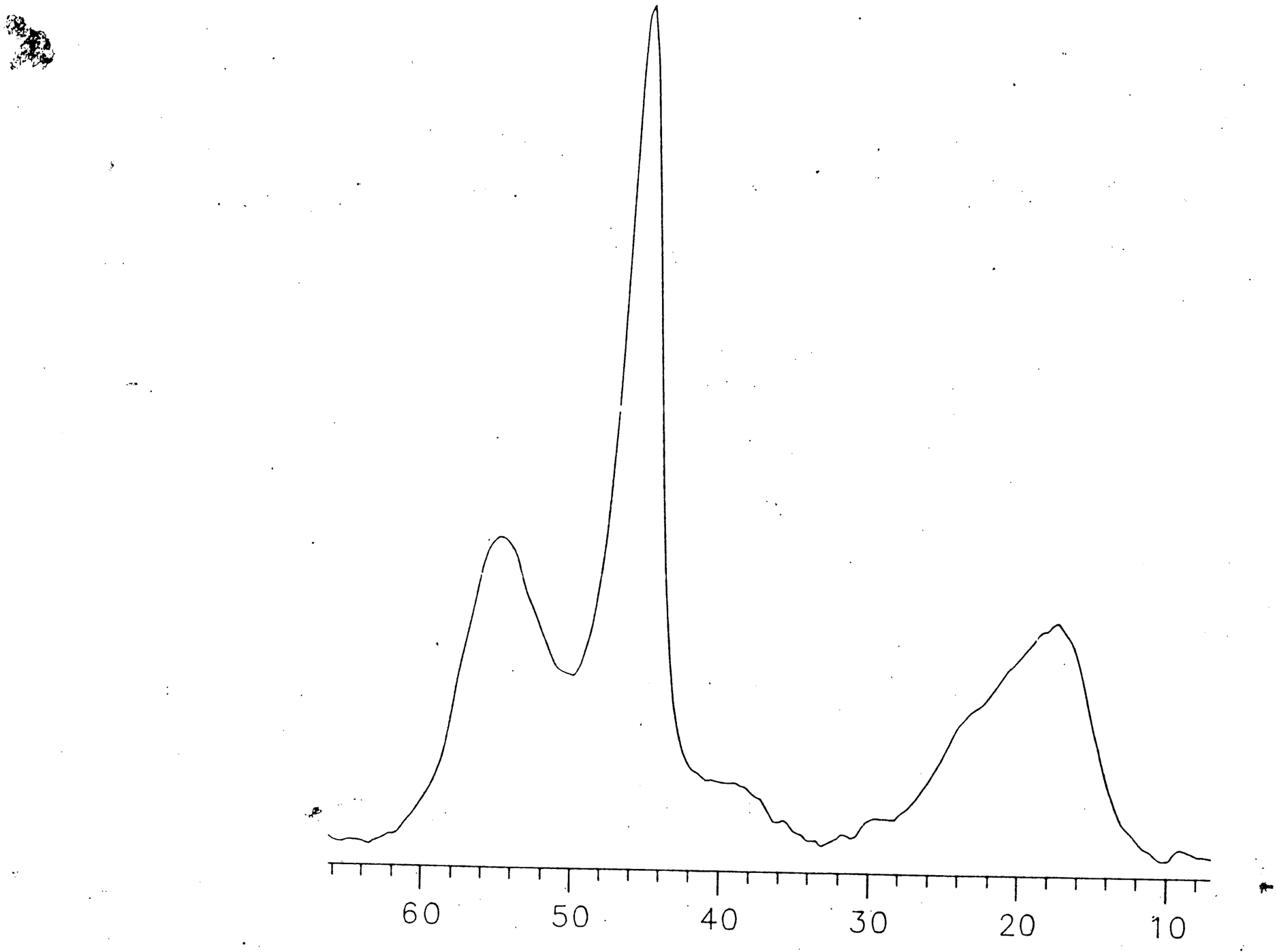


Figure 3-19: Expansion of the Fig. 3-18 at 10-60 ppm Chemical Shift

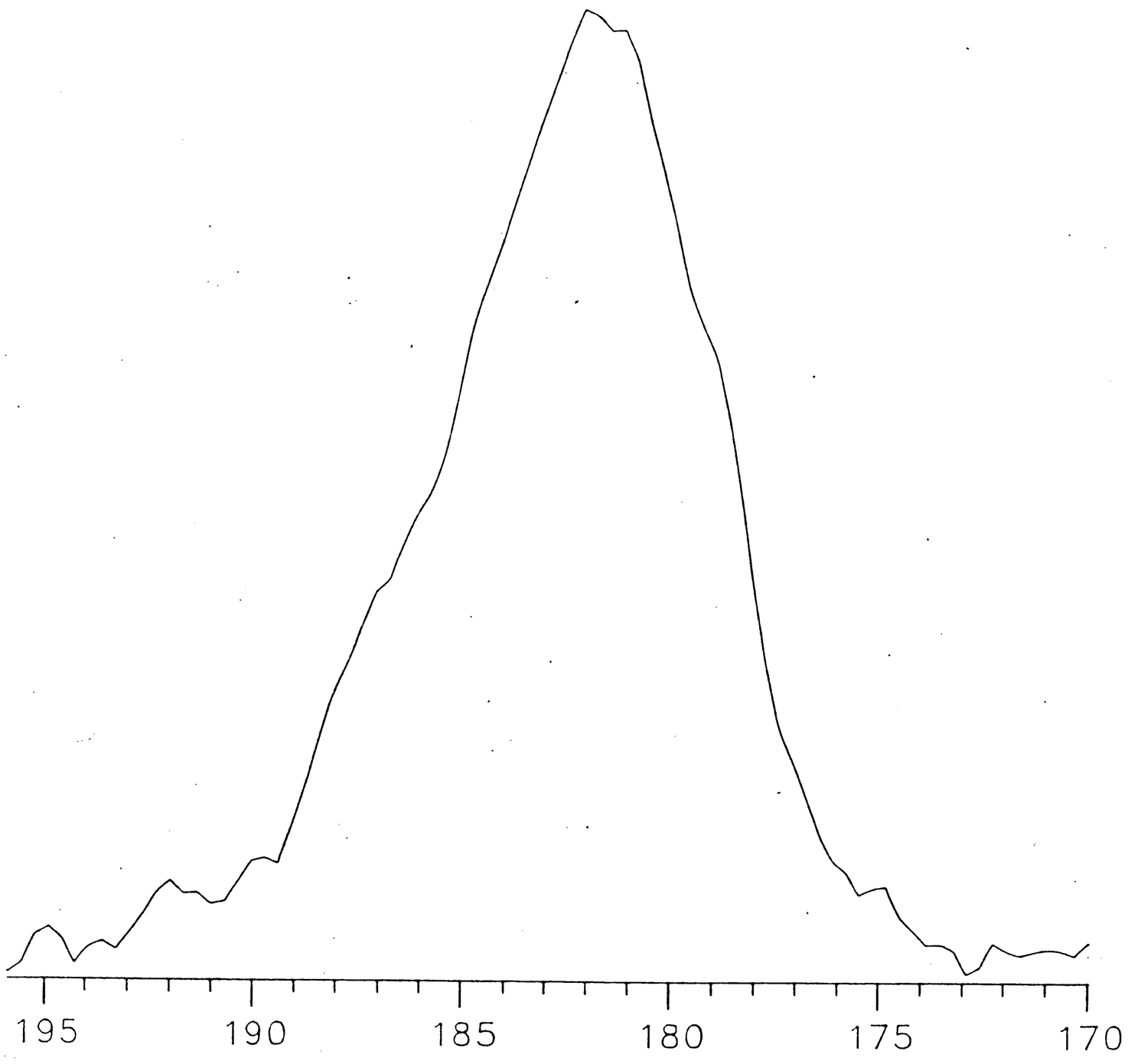


Figure 3-20: Expansion of the Fig. 3-18 at 170-190 ppm Chemical Shift

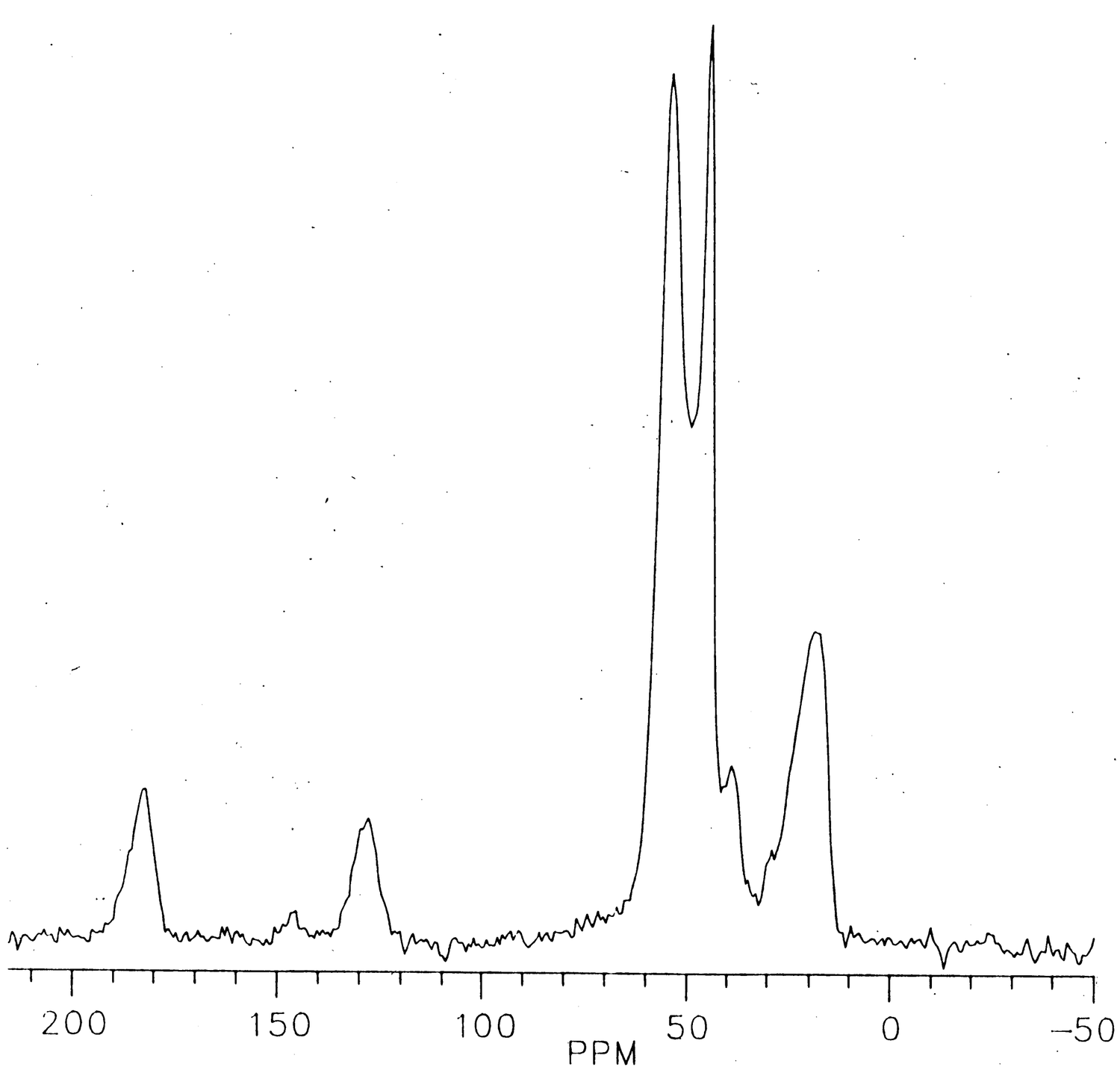


Figure 3-21: ^{13}C NMR Spectrum of Lead Loaded DP-1 Resin at pH 5.5

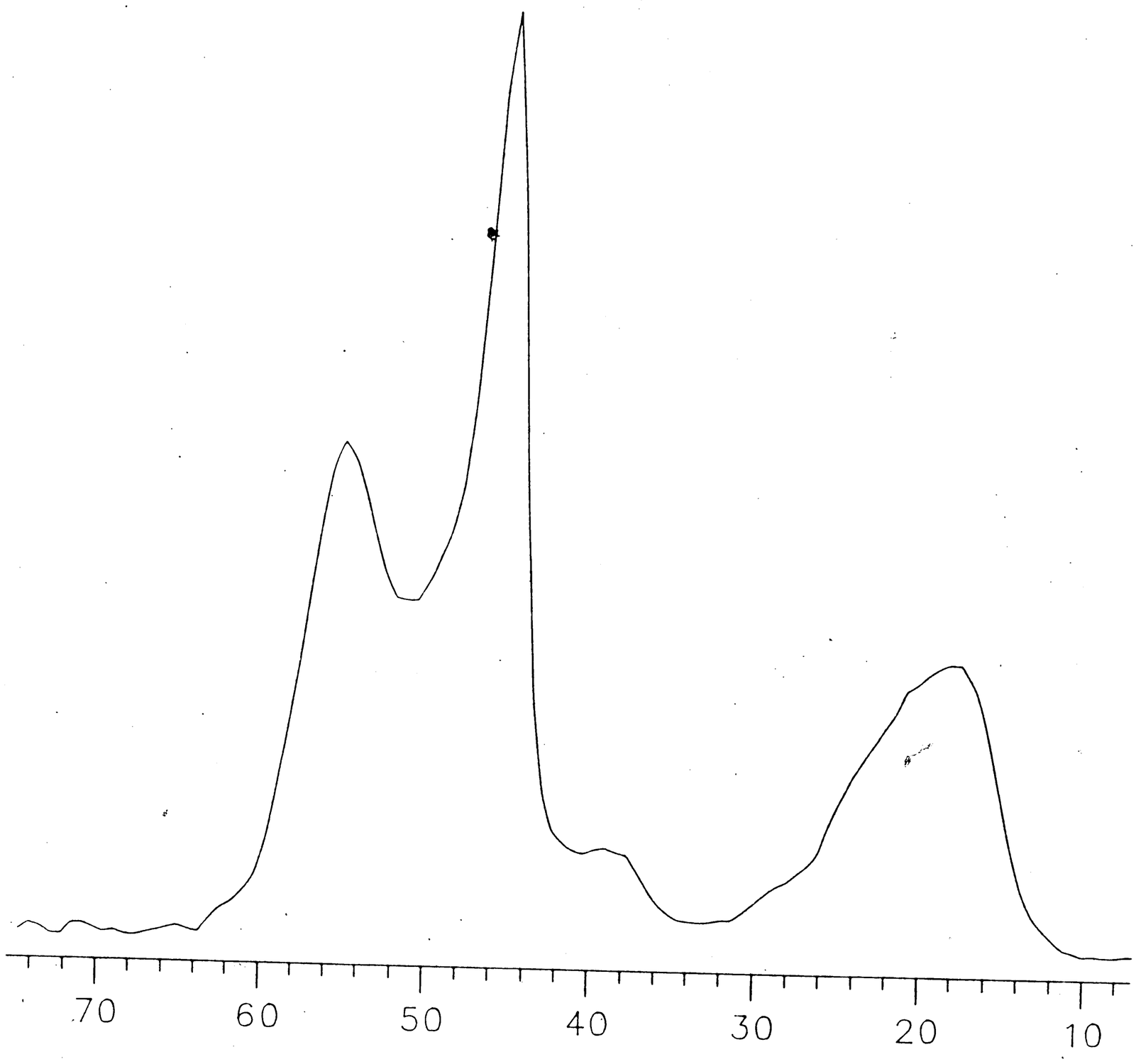


Figure 3-22: Expansion of the NMR Spectra of Fig. 3-21 at 10-60 ppm Chemical Shift

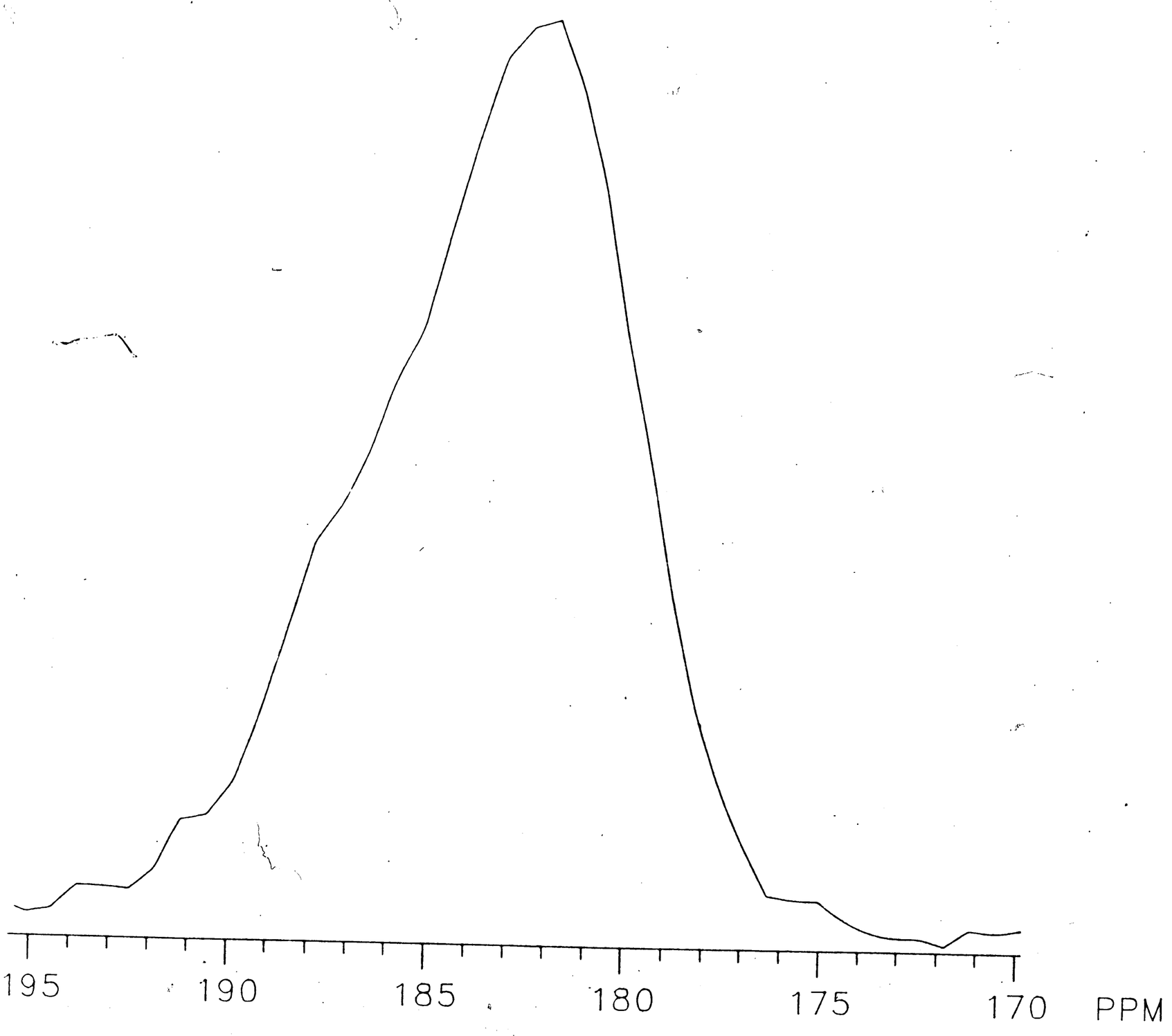


Figure 3-23: Expansion of the NMR Spectra of Fig. 3-21 at 170-190 ppm Chemical Shift

The titration (ref. Appendix U for the experimental data) of Bio-Rex 70 with lead at pH 4.0 and sodium nitrate concentration of 0.11M is presented in Fig. 3-27. This titration curve shows the presence of more than one independent class of binding site in the resin. Thus even at pH 4.0 covalent binding is evident in the case of lead in addition to the ion exchange type of reaction. The solution of Eqs. (3.12) to (3.15) gives the value of k_1, k_2, n_1 and n_2 as 10203.48, 627.77, 0.024 and 0.206 respectively showing a predominant covalent interaction of oxygen atoms. This result is in coformance with the predictions obtained from the ^{13}C NMR spectra. The overall complexation constant at pH 4.0 for the lead by the carboxylate resin works out as 6.41E6. The lead capacity of the DP-1 resin, obtained by passing through a small glass column a solution of lead nitrate containing 235 mg/l lead at pH 5.4, was observed as 12.78 meq per gm of resin in contrast to the sodium capacity of the same as 8.5 meq/gm ata pH of 8.4. This higher capacity of resin with lead even at a lower pH also verifies the presence of covalent bonding between the carboxylate oxygen atoms and the metal.

3.2.3 Binding of Cadmium, Nickel and Zinc by Carboxylates

The diffractometry data of Harrison and Trotter [58] shows that cadmium diacetate dihydrate, $Cd(CH_3COO)_2.(H_2O)_2$, contains acetate groups that are monatomically bridging as presented in Fig. 3-28. Unlike copper and lead acetate where each copper and lead atom is covalently bonded to four and eight oxygen atoms respectively, in cadmium diacetate dihydrate the cadmium is coordinated to seven oxygen atoms. The coordination is best described by a distorted square base-trigonal cap geometry.

The X ray structural determination of the crystal zinc acetate dihydrate, $Zn(CH_3COO)_2 \cdot 2H_2O$, has been carried out by Van Niekerk, Schoening and

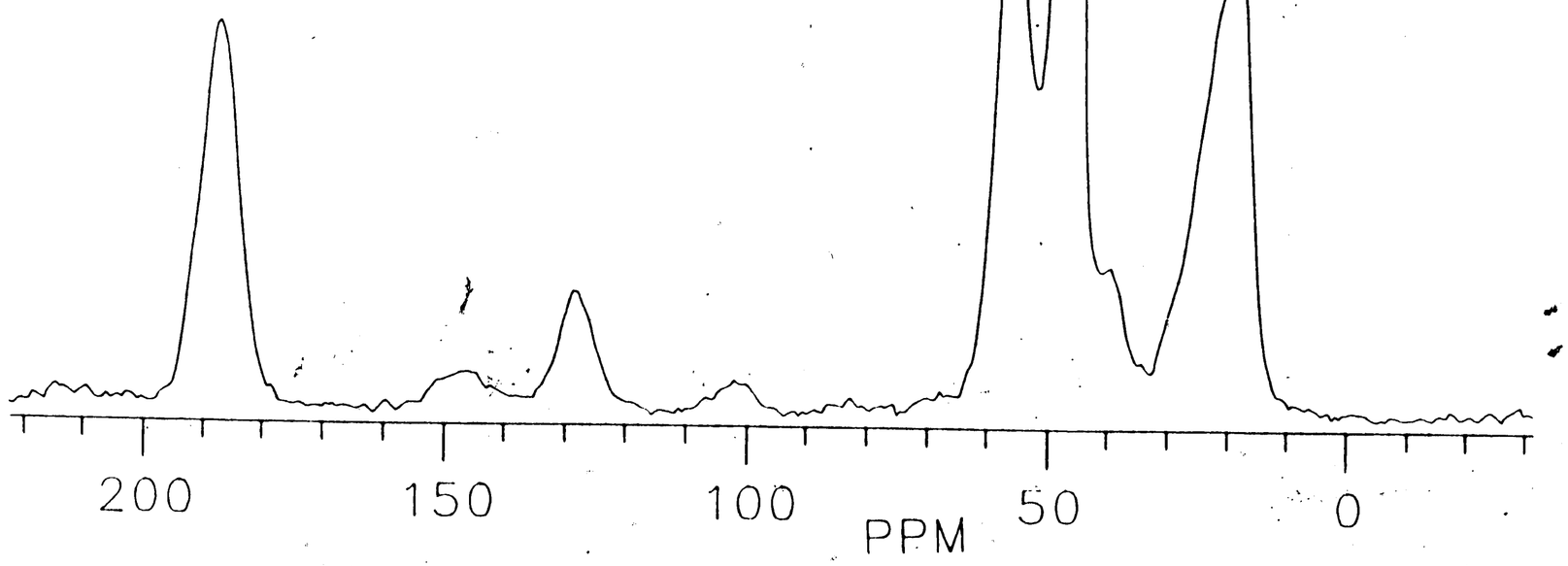


Figure 3-24: ^{13}C NMR Spectrum of DP-1 Resin Loaded with Calcium at pH 5.5

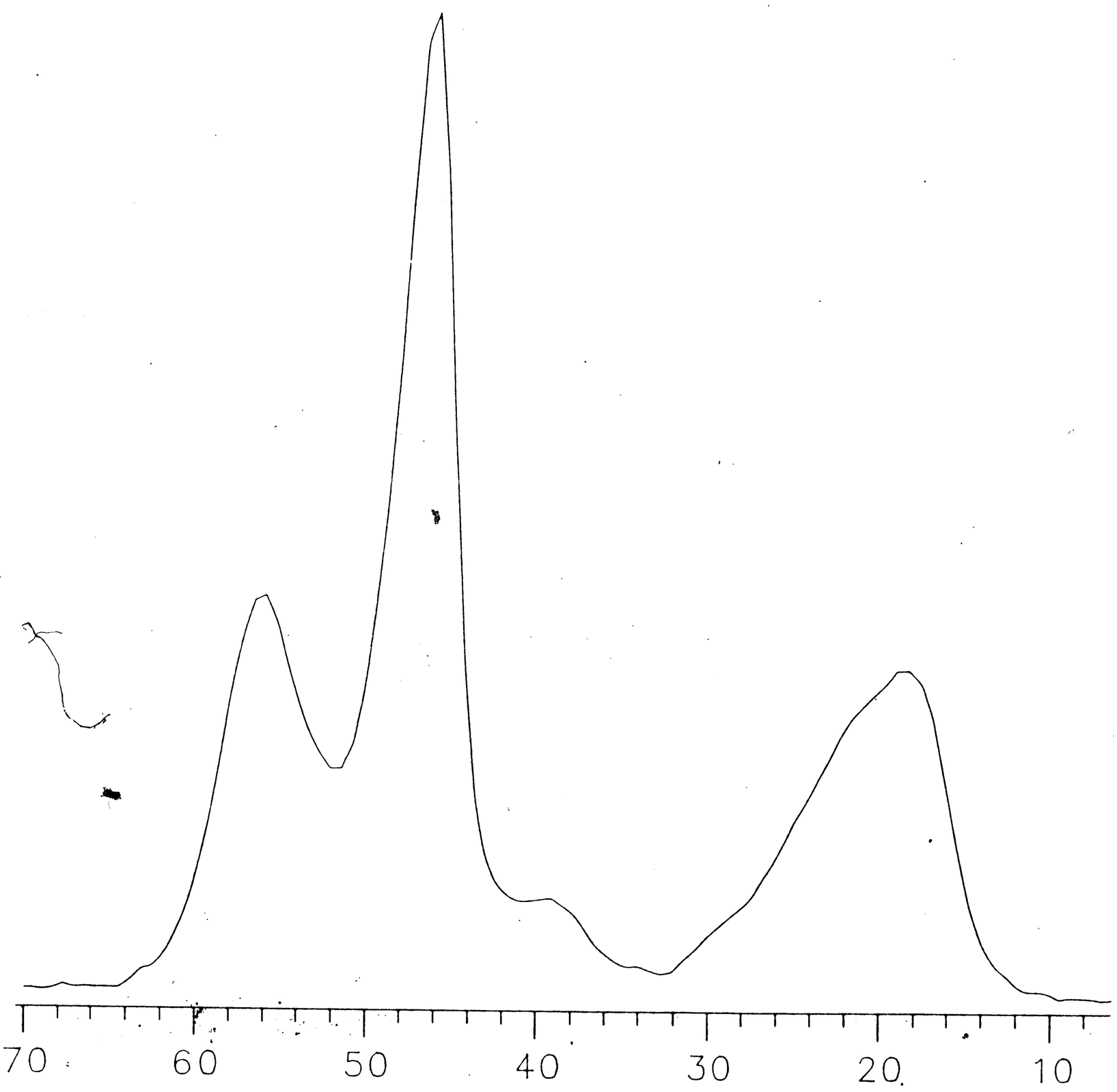


Figure 3-25: Expansion of the NMR Spectra of Fig. 3-24 at 10-60 ppm of Chemical Shift

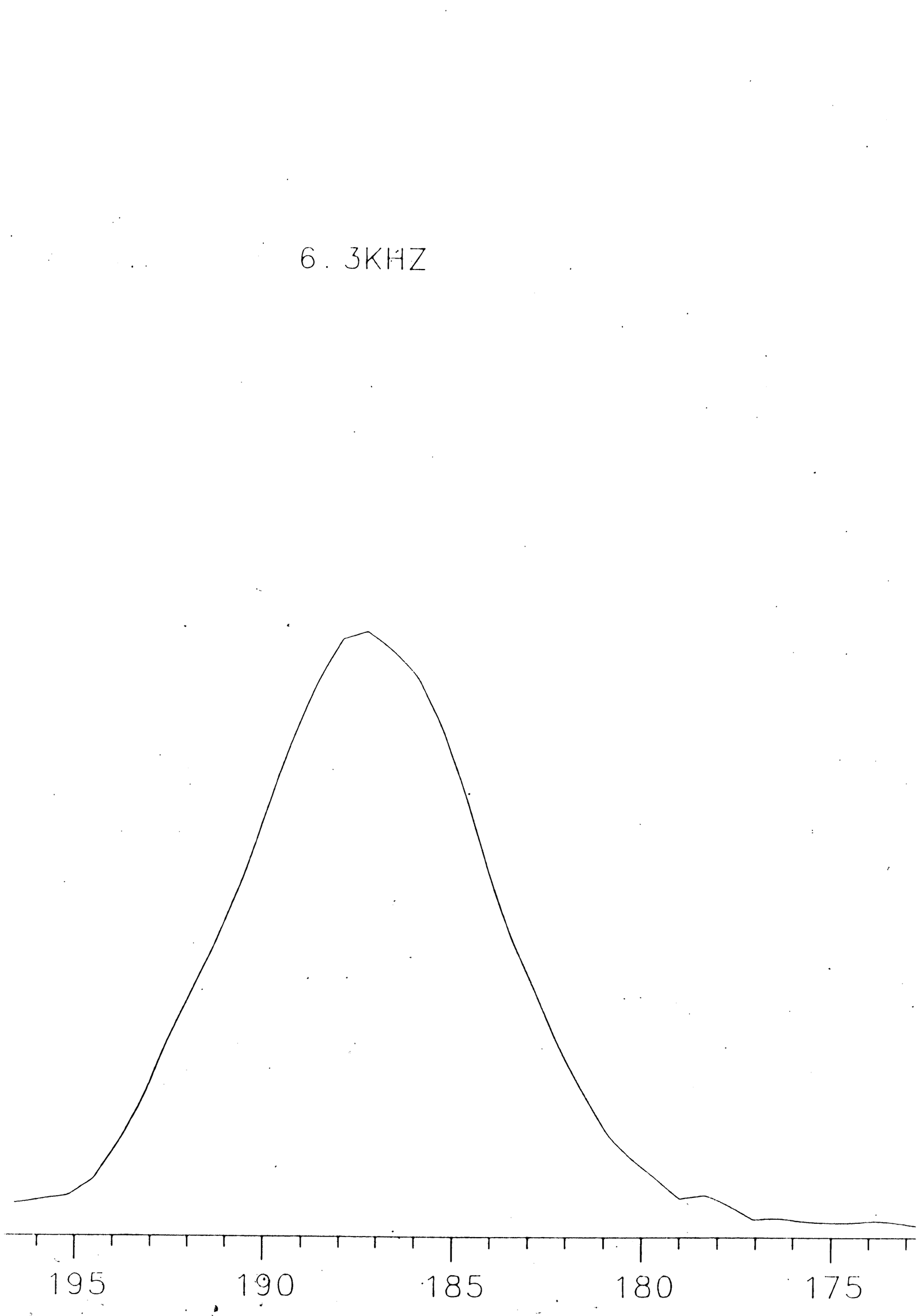


Figure 3-26: Expansion of the NMR Spectra of Fig. 3-24 at 170-190 ppm of Chemical Shift

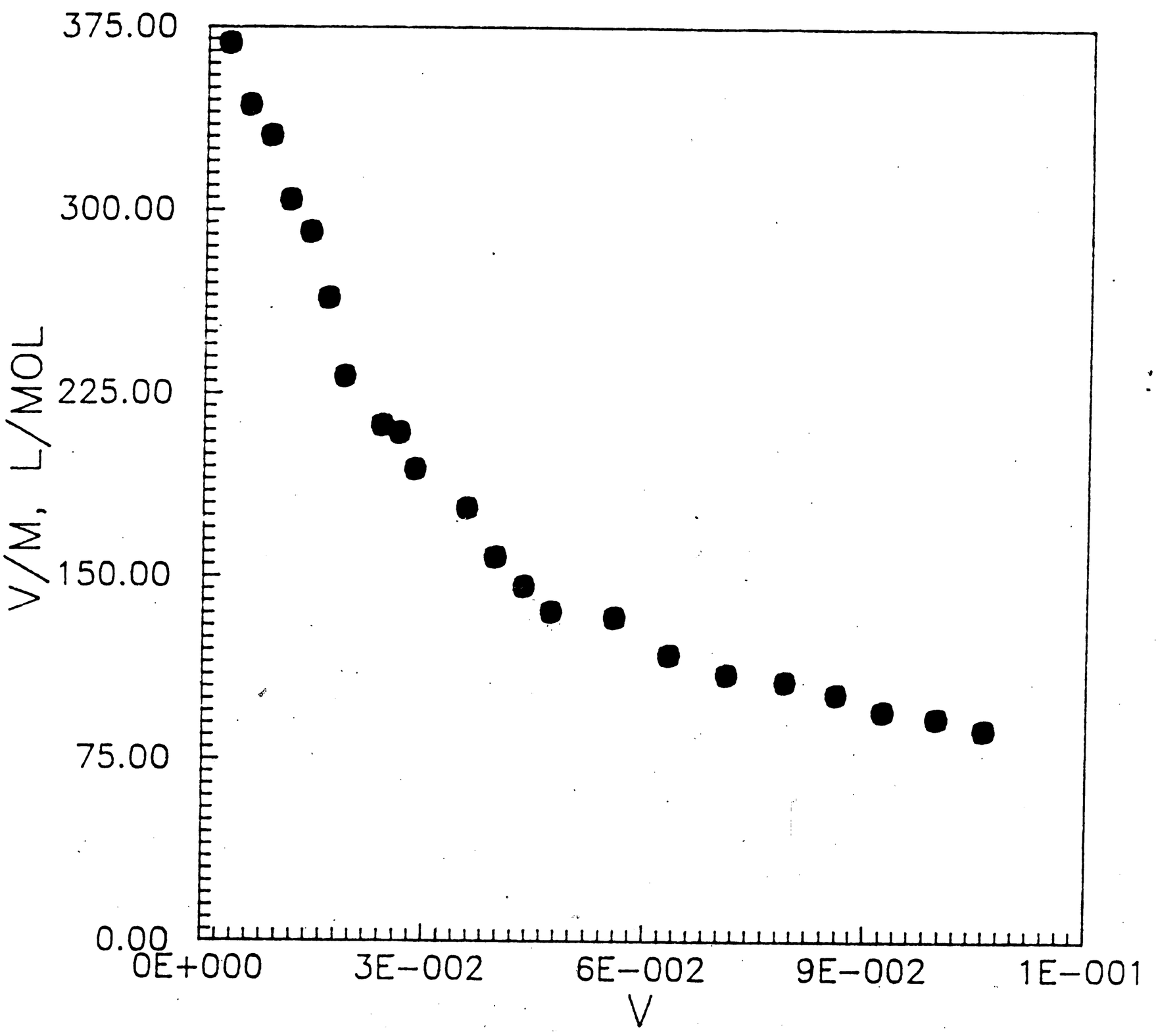


Figure 3-27: Titration of Bio-Rex 70 with Lead at pH 4.0 with 0.11M Sodium Nitrate

Talbot [55] and it shows that the compound contains chelating acetate groups and a distorted octahedral geometry around the zinc atom, being completed by two water molecules. The nearest six neighbours of a zinc atom are the four oxygen atoms and two water molecules. The above investigators also observed the presence of strong hydrogen bonding through water molecule in the formula units.

The X ray examination of the crystal structure of nickel acetate, $Ni(CH_3COO)_2.4H_2O$ has been carried out by Van Niekerk and Schoening [60]. In this crystal structure the metal atom is surrounded octahedrally by four water molecules and by two oxygen atoms which belong to two different acetate groups. This octahedral bonds are ionic in character and in the structure, the formula unit are firmly linked by a three dimensional network of hydrogen bonds. Based on their study on this crystal structure, Van Niekerk and Schoening suggested that one oxygen atom of an acetate group is linked by two hydrogen bonds to two water molecules, while the other oxygen atom makes one hydrogen bond to a water molecule and also an ionic bond to the doubly charged metal ion.

3.3 METAL BINDING MECHANISM OF RESIN WITH IDA FUNCTIONALITY

Unlike carboxylate ligand, little information is available regarding the nature of bonding between iminodiacetate (IDA) groups and metals. This functional group is a polydentate ligand because each molecule contains four donor oxygen atoms and one donor nitrogen atom. Chaberek and Martell [10] has suggested the binding mechanism of iminodiacetic acid with copper(II) as cooperative type and the same is schematically presented in Fig. 3-29.

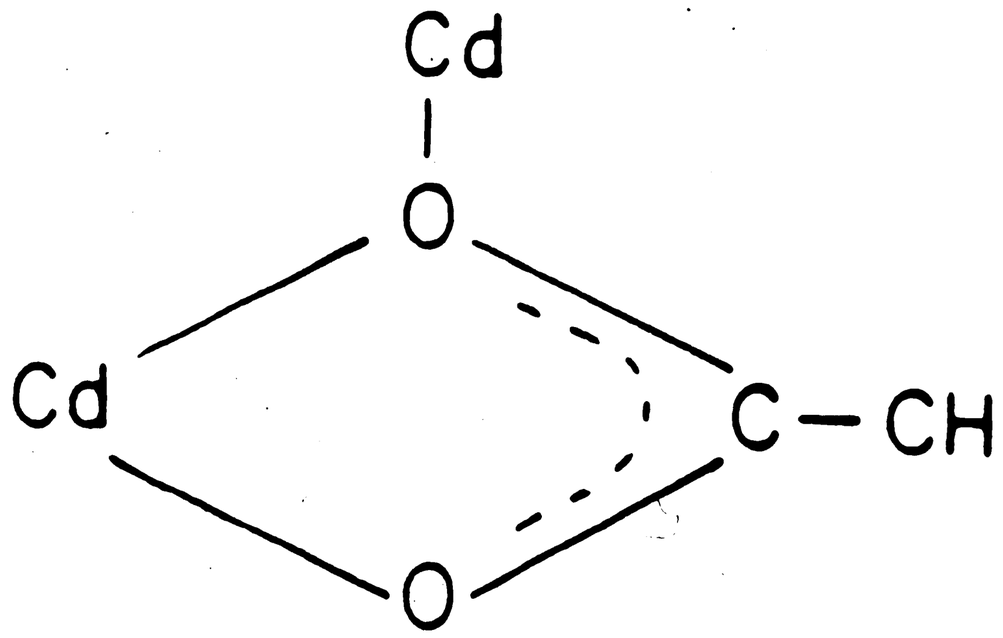


Figure 3-28: Structure of Cadmium Diacetate Dihydrate

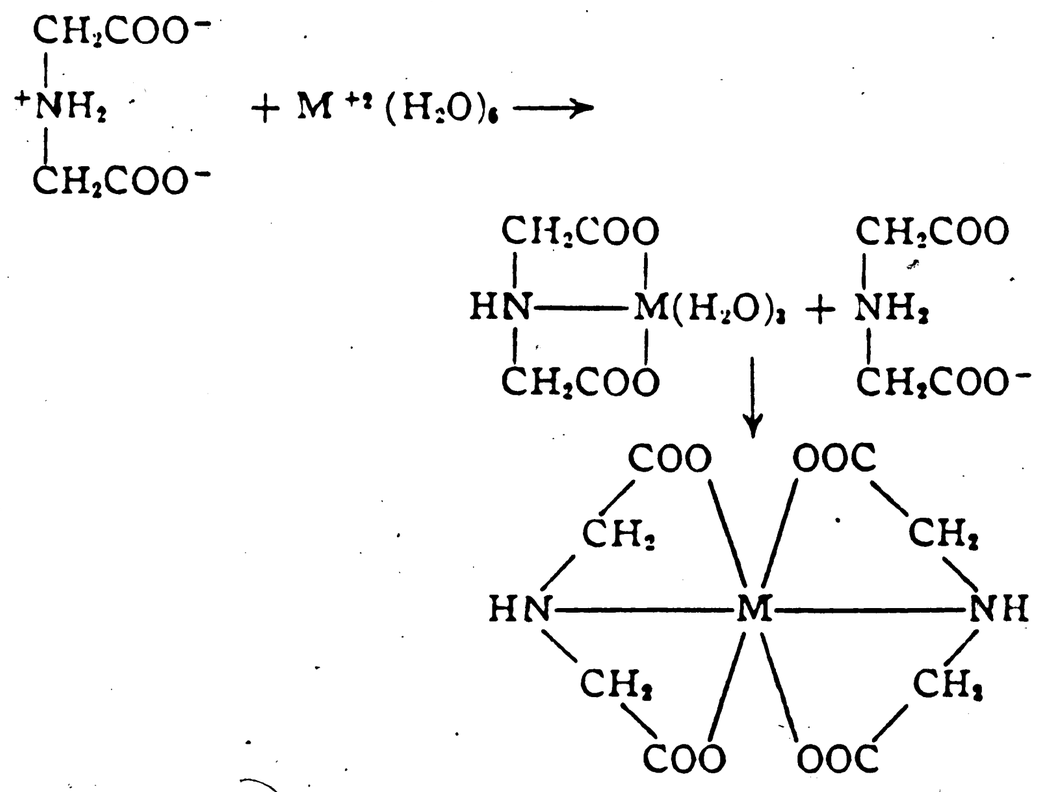


Figure 3-29: Schematic Arrangement of Copper(II) and IDA Bonding

3.3.1 Experimental Study for Binding Mechanism between Copper(II) and IDA Functional Groups

Chelex-100 resin with 200-400 mesh size was titrated with copper nitrate solution containing 0.11M sodium nitrate at pH 4.0 (for experimental data ref. Appendix V). The $\frac{v}{[M]}$ vs v plot, the Scatchard plot of this titration is presented in Fig. 3-30. This plot is analogous to Fig. 3-2 showing the presence of two independent classes of binding sites into the resin molecule.

In the case of carboxylate resin at pH 4.0, only one class of binding site was present and that binding site is responsible for ion exchange type interaction between the metal and the oxygen atom. Since in the case of iminodiacetate resin at pH 4.0 two independent binding class is present, the one being the oxygen atom and the other is definitely the nitrogen donor atom in the functionality. The k_1, k_2, n_1 and n_2 parameters, calculated from Eqs. (3.12) to (3.15), work out as 0.406, 0.174, 4.76E5 and 8.39E2 respectively. The overall complexation constant at pH 4.0 for this resin with copper works out as 3.99E8.

Thus incorporating the donor nitrogen atom into the resin functionality, the stability constant of the resin has increased from 137.29 in the case of the carboxylate resin, Bio-Rex 70, to 3.99E8 in the case of Chelex-100. This significance increase in the stability constant of Chelex-100 explains its higher selectivity for the copper ion at pH 4.0 over than that of the carboxylate resin.

3.4 OBSERVATIONS :

The significant findings of the above study are:

- For the copper-polymer binding at pH 4.0, in the case of carboxylate resin, only one class of binding site is present with a stability constant of 137.29 at 0.048M sodium nitrate concentration.

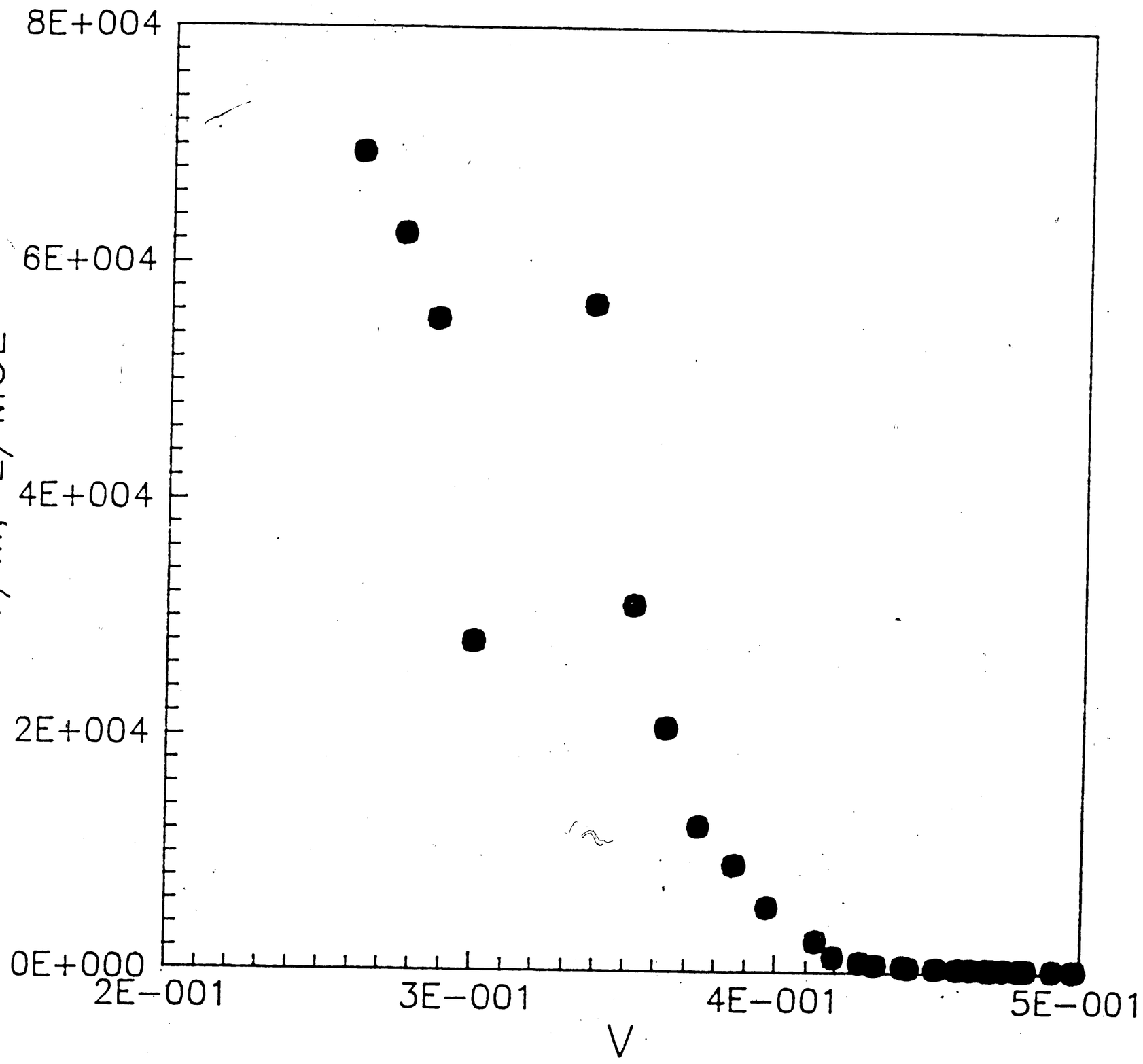


Figure 3-30: Titration of Chelex-100 with Copper at pH 4.0 with 0.11M Sodium Nitrate

- At pH 5.5, experimental data indicates that more than one class of binding site is present in the carboxylate copolymer to attach the copper ion. The overall complexation constant between the resin and copper(II) were observed as 2.127×10^7 and 1.42×10^7 with a sodium nitrate concentration of 0.048M and 0.11M respectively.

- At pH 4.0, the experimental results show that more than one class of binding site is present in the carboxylate resin to bind lead. The stability constant of lead-polymer is 6.41×10^6 at pH 4.0 with a sodium nitrate concentration of 0.11M.

- From the literature study for the interaction between the carboxylate and the other metals [58, 55, 60], it is observed that the structural configuration of the metals differ significantly within the compound and also in the bridging with the neighbouring oxygen atoms.

- In the case of copper binding with the resin containing iminodiacetate functionality, experimental data reveals the presence of more than one class of binding site in the resin. The overall complexation constant for the binding of copper(II) and the copolymer was observed as 3.99×10^8.

Chapter 4
MODIFYING METAL ION SELECTIVITY OF CHELATING RESINS BY LIGAND AND pH

4.1 INFLUENCE OF AXIAL LIGANDS ON COORDINATED COMPLEX

The dimeric copper(II) carboxylate adducts have the general formula $[Cu(RCOO)_2 . L]_2$ and the schematic structure of these complexes are given in Fig. 4-1. In this structure and the chemical formula R is a substituent in the methyl group of carboxylic acids and L is an apical ligand.

In an attempt to correlate the pK_a values of the acetic acids, with the interaction between copper(II) and carboxylic acids, it was observed [42] that a tendency for the formation of mononuclear molecules, from the binuclear copper-carboxylate dimer, is enhanced as the number of halogen substituents is increased. The introduction of one, two or three halogeno atoms in the methyl group of acetic acid results in an increase in the acid strength in the order $XCH_2COO^- < X_2CHCOO^- < X_3CCOO^-$ (X is F, Cl, Br or I) as a result of α-electron attracting effect of the halogen atom and produces a comparatively decreasing O-M interaction by decreasing the electron density of the oxygen atoms; thus weakening the metal-oxygen covalent bond through which the metal binding mechanism of the carboxylates operates. Other substituents in the methyl groups have also been studied [43] and the general observations are

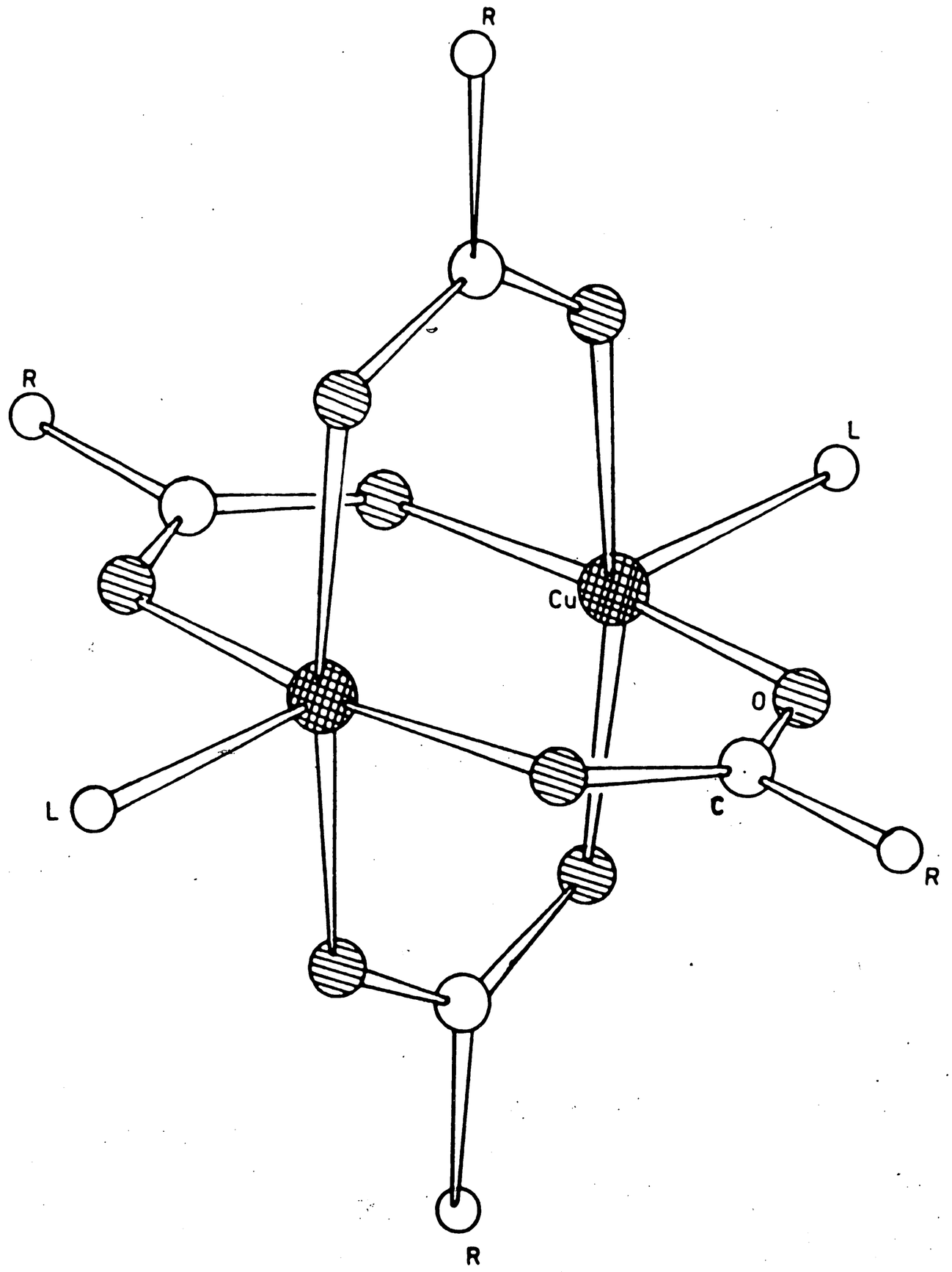


Figure 4-1: Schematic Structure of Binuclear Copper(II) Dimer with Axial Ligand

that as the carboxylate substituent R becomes a stronger electron donor, the metal-oxygen covalent bond becomes weaker.

The apical ligand L also plays an important role in the metal-oxygen bridging of the carboxylates. In the dimeric copper(II) carboxylates, when the L $\rightarrow$ Cu donation becomes stronger, the covalent Cu - O bonds in the CuO_4 basal plane become weaker to maintain the electroneutrality over the whole molecule. A weaker L $\rightarrow$ Cu donation will cause a stronger ligand field of the four carboxylato-oxygen atoms around the metal ions [31]. Thus the metal-oxygen interaction decreases according to the series of terminal ligands : aniline < water < anhydrous < pyridine < picolines ~ SCN^- ~ ethanol < dioxane. With a stronger ligand L, the metal shifts from the CuO_4 basal plane to the ligand site.

The DP-1 resin was equilibrated with a solution containing lead and ethylenediamine with 1:50 mole ratio at pH 5.5. The equilibrated resin was thereafter washed with deionized water and air dried. The ^{13}C NMR spectrum of this resin is given in Fig. 4-2. Figure 4-3 and Figure 4-4 are the expansion of this NMR spectrum at 175-195 ppm chemical shift and 10-70 ppm chemical shift respectively. From Fig. 4-3 it is observed that the chemical shift of the carboxylate is approximately 3.5 ppm from the normal chemical shift of the carboxylate (as shown in Chapter 3). The ethylene group of the ligand, ethylenediamine, shows up strongly at its normal chemical shift i.e., at 41 ppm (ref. Fig. 4-4). These Figures show that the lead has shifted towards the ligand site from the binding oxygen sites in the resin due to the weaker interaction between the metal and oxygen in the presence of a stronger ligand.

Thus, the metal ion selectivity of a chelating resin can be altered by (i) making a judicious choice of the substituent in the methyl group of the polymer or the neighbouring groups to carboxylates (ii) selecting a suitable ligand in the aqueous phase so that the metal-ligand interaction becomes much stronger than

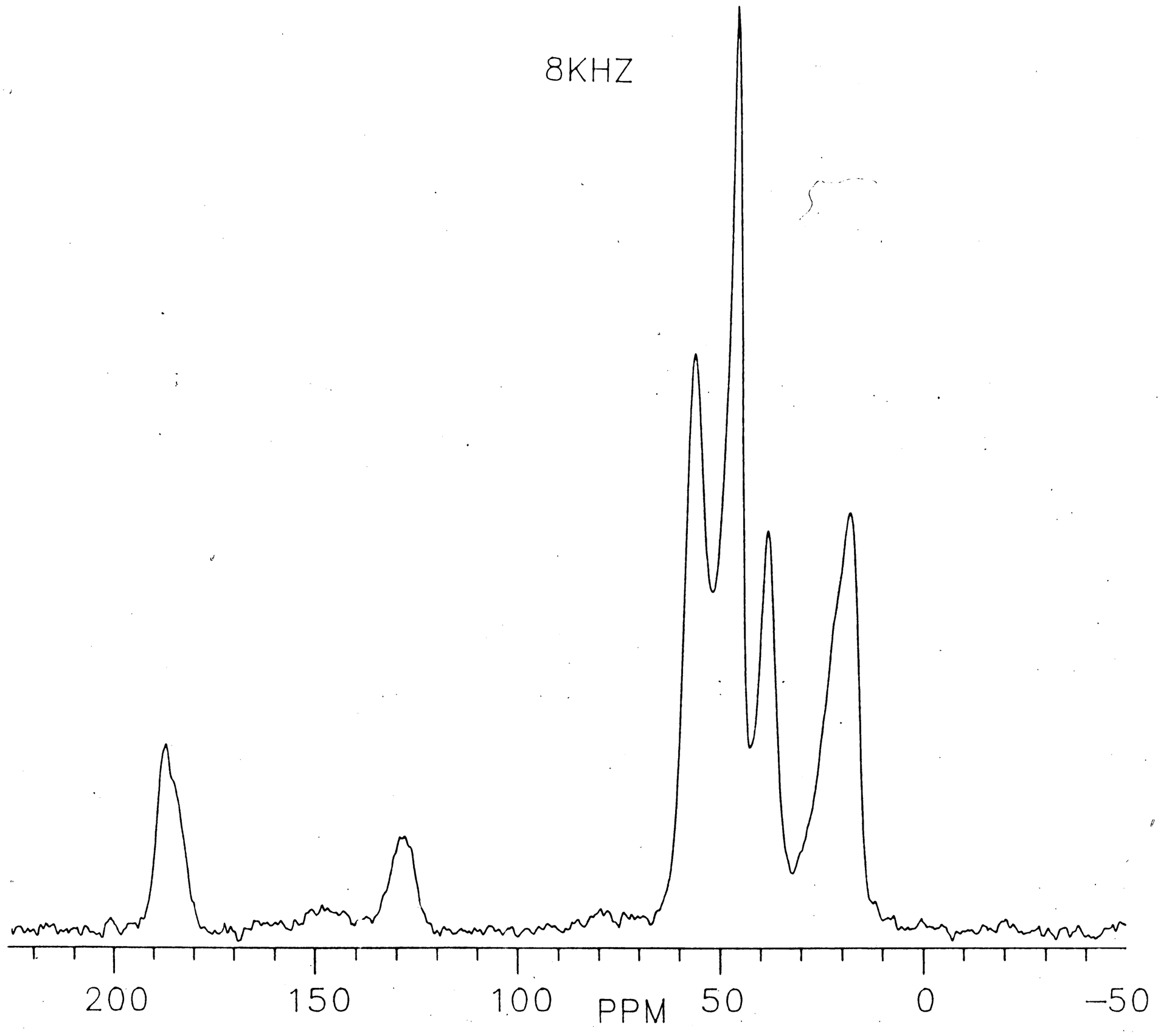


Figure 4-2: ^{13}C NMR Spectrum of DP-1 Resin equilibrated with Lead and Ethylenediamine with 1:50 Molar Ratio at pH 5.5

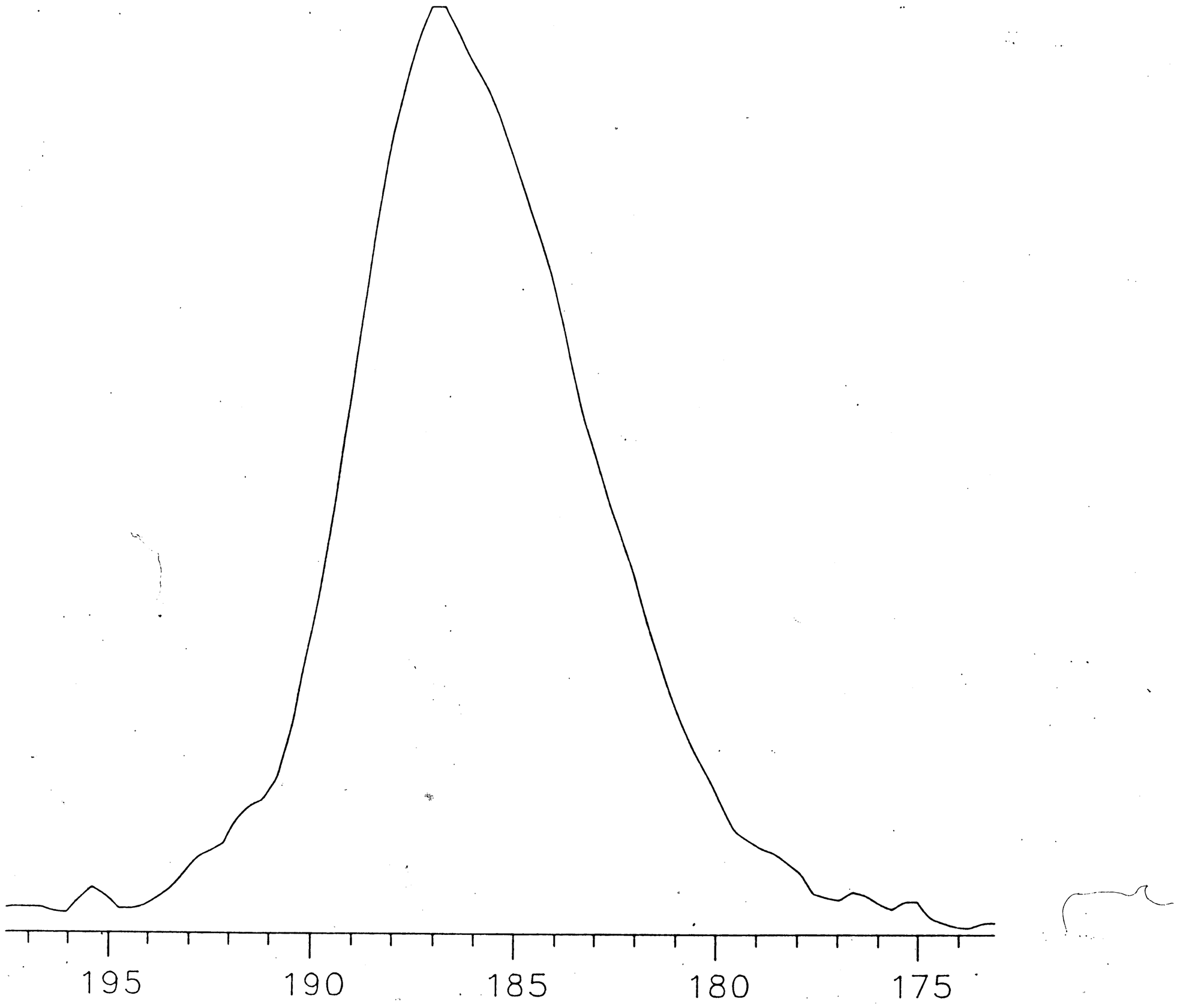


Figure 4-3: Expansion of the NMR Spectrum of Fig. 4-2 at 175-195 ppm

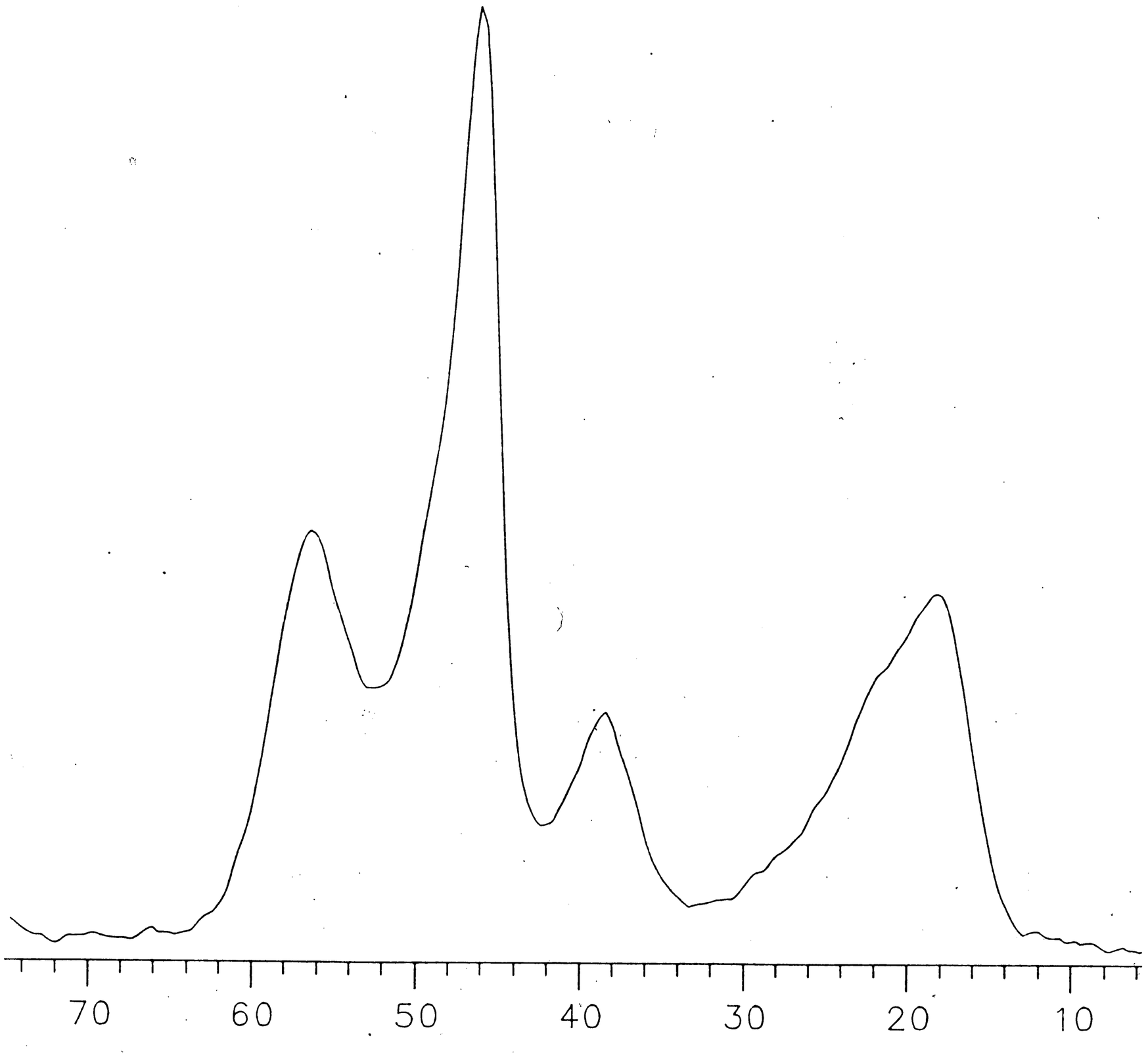


Figure 4-4: Expansion of the NMR Spectrum of Fig. 4-2 at 10-60 ppm

the metal-oxygen bonding in the carboxylates. In a commercially available chelating resin there is little scope of modifying the resin structure by making a substituent in the neighbouring groups of the functional sites. Hence, from application point of view, the second alternative i.e., the choice of incorporation of a stronger ligand in the aqueous phase seems convenient.

4.1.1 Selection of Ligand

As discussed already, the stronger the ability of the donar ligand, the less will be the interaction between the chelating group in the resin and the metal. In an ion exchange application, for the individual separation of metals from a mixed waste, the choice of the ligand is critical. The coordination complex formation ability of the ligand, with the metals present in the waste, should differ by several orders of magnitude so that the weakly cordinated metal-ligand complex is adsorbed onto the chelating resin and thereby separated while the strongly coordinated metal-ligand complex does not undergo ion exchange reaction.

In the study, ethylenediamine (En) has been selected as a ligand because it forms coordination complexes with all the five metals studied and its relative ability to form coordinated complex with the metals are : copper > nickel > zinc > cadmium > lead. En is a colourless liquid and soluble in water. Its density, boiling point and melting point are 0.899, 116.5^{0}C and 8.5^{0}C respectively [13]. The pK_{b1} and pK_{b2} values of ethylenediamine are 10.712 and 7.564 respectively [13]. From the application point of view, another advantage of using ethylenediamine is that it can be recovered from the aqueous phase easily by suitable separation processes [11], as indicated in Fig. 4-5 and can be recycled in the system; thus it will not impart any dissolved impurity into the system after the recovery goal is accomplished.

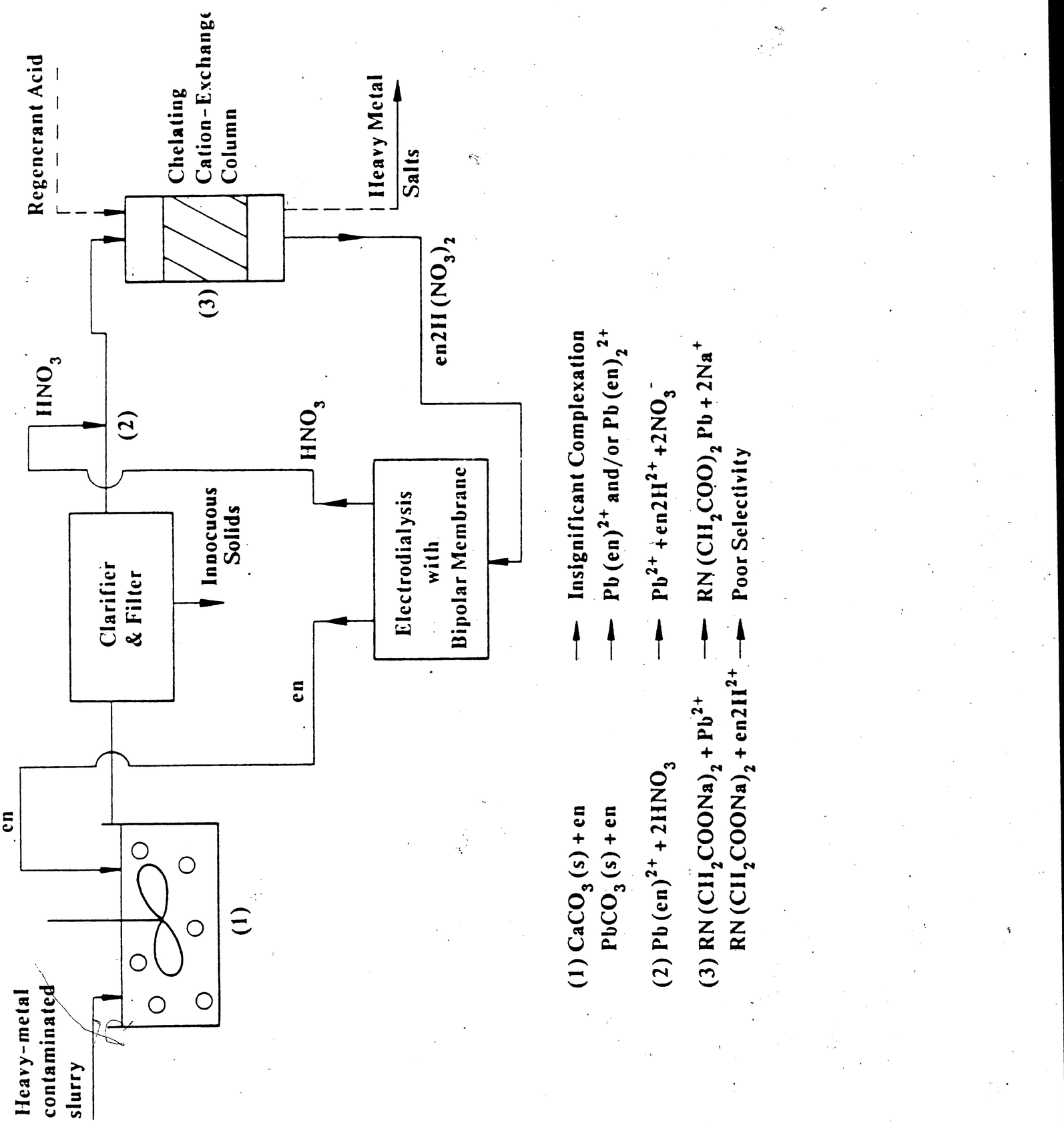


Figure 4-5: Schematic Process for the Recovery of En from an Effluent

4.2 THEORETICAL ASPECTS OF En-METAL REACTIONS

Ethylenediamine speciates in water and its speciation is dependent on the aqueous phase pH. En reacts with all the metal ions studied to form coordination complexes. En forms two coordination complexes with the copper and lead ions; and, with each of the remaining metal ions En forms three coordination complexes. In the theorectical study for the En-metal reactions, analysis has been restricted upto two coordination complexes for all the metals.

4.2.1 Speciation of En in Water

The speciation reactions of En in water can be given as :

$$En + H^+ = EnH^+ , \quad K_{ST1} = 10^{9.93} \tag{4.1}$$

$$EnH^+ + H^+ = EnH_2^{2+} , \quad K_{ST2} = 10^{6.85} \tag{4.2}$$

Where K_{ST1} and K_{ST2} are the first and second stability constant data [44] of En with the hydrogen ion.

4.2.2 Complexation Reactions between Cadmium and En

The two complexation reactions between the cadmium ion and En are given as :

$$Cd^{2+} + En = Cd(En)^{2+} , \quad K_{ST1} = 10^{5.4} \tag{4.3}$$

$$Cd(En)^{2+} + En = Cd(En)_2^{2+} , \quad K_{ST2} = 10^{4.5} \tag{4.4}$$

Where K_{ST1} and K_{ST2} are the first and second stability constant data [44] for the complexation reaction between cadmium and En.

4.2.3 Complexation Reaction between Copper and En

The first and the second stability constant data [44] along with coordination reactions between copper and En can be given as :

$$Cu^{2+} + En = Cu(En)^{2+}, \quad K_{ST1} = 10^{10.5} \tag{4.5}$$

$$Cu(En)^{2+} + En = Cu(En)_2^{2+}, \quad K_{ST2} = 10^{9.1} \tag{4.6}$$

4.2.4 Complexation Reactions between Nickel and En

The complexation reactions along with first and second stability constant data [44] for the nickel with En are given as :

$$Ni^{2+} + En = Ni(En)^{2+}, \quad K_{ST1} = 10^{7.4} \tag{4.7}$$

$$Ni(En)^{2+} + En = Ni(En)_2^{2+}, \quad K_{ST2} = 10^{6.2} \tag{4.8}$$

4.2.5 Coordination Reactions between Lead and En

The first and the second stability constant data [44] between lead ion and En along with the complexation reactions are given as :

$$Pb^{2+} + En = Pb(En)^{2+}, \quad K_{ST1} = 10^{7.0} \tag{4.9}$$

$$Pb(En)^{2+} + En = Pb(En)_2^{2+}, \quad K_{ST2} = 10^{1.5} \tag{4.10}$$

4.2.6 Complexation Reactions between Zinc and En

The coordination reactions between the zinc ion and En along with the first and the second stability constant data [44] of the complexation reactions can be represented as:

$$Zn^{2+} + En = Zn(En)^{2+}, \quad K_{ST1} = 10^{5.7} \tag{4.11}$$

$$Zn(En)^{2+} + En = Zn(en)_2{}^{2+}, \quad K_{ST2} = 10^{4.9} \tag{4.12}$$

4.2.7 Effect of En Concentration and pH on a Binary System of Metal Ions

It is evident from Eq. (4.1) and Eq. (4.2) that the complexation reaction between metal and En will be pH dependent since speciation of En is pH dependent. Based on the coordination reactions, between metal ions and En given by Eq. (4.3) to Eq. (4.12), theoretical calculation can be performed for the free concentration of individual metal ions in the aqueous phase at a given pH. A binary system, comprising of two metal ions at a time, has been considered. However, for such a binary system, three more Eqs. needed to be formed from the mass balance relationship.

For the each binary system considered, individual metal ion concentration has been considered as 1.0 mole/l. En is added into the system in steps to attain a maximum total En concentration of 100.0 mole/lit in the aqueous phase. For the theoretical calculation, it has been considered that the En addition will not alter the system volume and also will not have any dilution effect on aqueous phase metal ion concentration. It is assumed that the concentration change of any species is solely attributable to the complexation reaction.

The mass balance relationship between the various possible aqueous species can be given as:

$$M_1^{2+} + M_1(En)^{2+} + M_1(En)_2^{2+} = M_{1T} \quad (4.13)$$

$$M_2^{2+} + M_2(En)^{2+} + M_2(En)_2^{2+} = M_{2T} \quad (4.14)$$

Where the first, second, third and the fourth term of Eq. (4.13) and Eq. (4.14) are respectively the concentration of free metal ion, the first complexation product, the second complexation product and the total metal ion concentration of the two different metals M_1 and M_2 respectively.

The third mass balance realtionship is for the component En and can be given as:

$$En + EnH^+ + EnH_2^{2+} + En^{2+}(M_1 + M_2) + 2.(En)_2^{2+}(M_1 + M_2) = En_T \quad (4.15)$$

Where, En_T is the total concentration (the amount added) of En in the system in mole/lit.

Eq. (4.1) and Eq. (4.2), the material balance Eq. (4.13) to Eq. (4.15) and the two complexation reaction Eqs., for each of the two metal ions considered, are then solved simultaneously to find out the distribution of the species at different En_T and pH. IMSL subroutines ZSPOW and LEQT1B have been used to solve the above Eqs.. Logarithimic concentration of the individual free metal ions vs En_T to total metal ion concentration ratio are then plotted at different pH for each of the possible binary combinations.

4.2.7.1 Cu - Cd - En System

The concentration of free metal ions for this system is presented in Fig. 4-6 and it is observed that at pH 4.0 the Cd^{2+} concentration remains almost unaltered (0.96 mole/l) even at the maximum concentration of 99 mole/l of En(total). The corresponding Cu^{2+} concentration is 0.97E-6 mole/l.

At pH 5.0, Cd ions also forms complexes with the En. The free Cd ion concentration is 0.145 mole/l at a total En concentration of 99 mole/l with corresponding Cu ion concentration as 1.02E-10 mole/l.

At pH 6.0, cadmium undergoes a significant reaction with the En and its free concentration drops sharply to 0.64E-4 mole/l at a total En concentration of 99 mole/l. The Cu ion concentration, at this En value, is 1.32E-14 mole/l.

At the En(total) concentration of 5.0 mols/lit, Cu ion concentration in the aqueous phase are 0.81E-3, 0.11E-6 and 0.46E-10 mols/lit at pH 4.0, 5.0 and 6.0 respectively. At all pH conditions and En(total) concentrations, Cu ion concentration is lower than Cd ion by several orders of magnitude.

4.2.7.2 Cu - Ni - En System

Ni ion forms complexes with En even at pH 4.0. At this pH and total En concentration of 99 mole/l, Ni and Cu ion concentration are 0.18 and 0.12E-5 mole/l respectively. At pH 5.0, Ni and Cu ion concentration are 1.E-4 and 0.1E-9 mole/l respectively with an En(total) concentration of 99 mole/l. Aqueous phase Ni ion concentration drops appreciably as the system pH is increased further. With a total En concentration of 99 mole/l at pH 6.0, the Ni and Cu ion concentration are 0.13E-7 and 0.13E-13 mole/l respectively.

At 11 mole/l En(total) concentration and at pH 4.0, 5.0, 6.0 the corresponding copper ion concentration is 1.13E-4, 1.73E-8 and 2.42E-12 mole/l respectively with corresponding Ni ion concentration of 0.73, 1.1E-2 and 2.4E-6 mole/l. The concentration profile of metal ions for this binary system is given in Fig. 4-7.

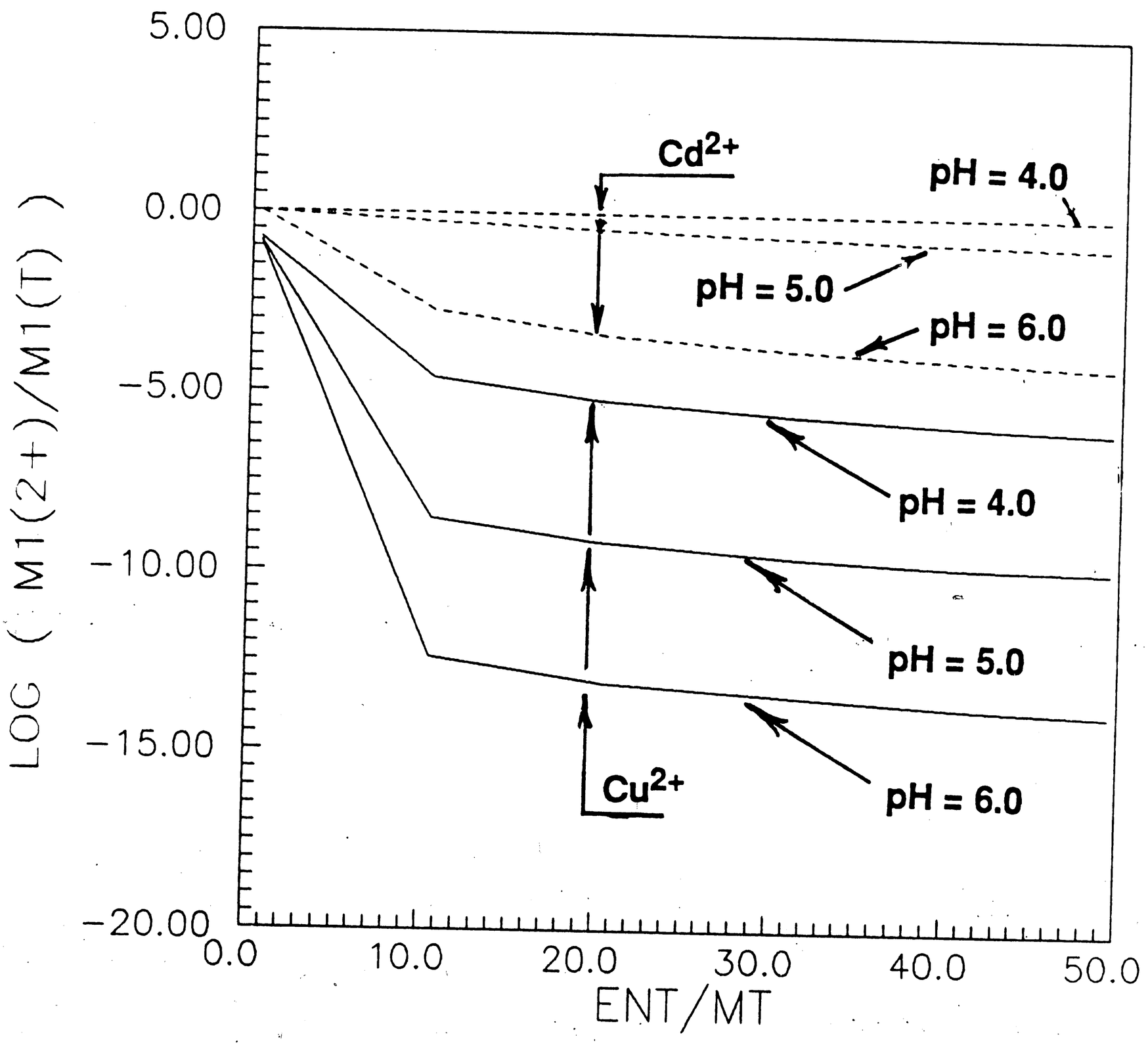


Figure 4-6: Effect of En and pH on a Binary System Containing 1 mole/l each of Cadmium(II) and Copper(II)

4.2.7.3 Cu - Pb - En System

The concentration of Pb ion and Cu ion at different pH and En concentration are plotted in Fig. 4-8. At pH 4.0, 5.0 and 6.0 with a total En concentration of 99 mole/l, Pb ion concentration is 0.385, 0.63E-2 and 0.69E-4 mole/l respectively with a corresponding Cu ion concentration of 0.98E-6, 0.1E-9 and 0.13E-13 mole/l.

At En (total) concentration of 11 mole/l and at pH 4.0, 5.0 and 6.0, the Cu ion concentration is 0.11E-3, 0.14E-7 and 0.18E-11 mole/l respectively. The Pb ion concentration, at these conditions, is 0.87, 0.7E-1 and 0.86E-3 mole/l respectively.

4.2.7.4 Cu - Zn - En System

The concentration diagram of Zn ion and Cu ion at various pH and En concentration is given in Fig. 4-9. At pH 4.0, 5.0 and 6.0 with En (total) concentration of 99 mole/l, Zn ion concentration is 0.92, 0.54E-1 and 0.13E-4 mole/l respectively. Corresponding Cu ion concentrations, at these conditions, are 0.97E-6, 0.1E-9 and 0.13E-13 mole/l respectively.

At a total En concentration of 11 mols/lit, Zn ion concentration is 0.99, 0.56 and 0.21E-2 mole/l at pH of 4.0, 5.0 and 6.0 respectively, with 0.11E-3, 0.13E-7 and 0.23E-11 mole/l as the corresponding Cu ion concentration.

4.2.7.5 Cd - Ni - En System

The Cd and Ni ion concentration has been plotted in Fig. 4-10 as a function of pH and En concentration. At pH of 4.0, 5.0 and 6.0, with an aqueous phase total En concentration of 99 mole/l, the Cd ion concentration is 0.96, 0.145 and 0.64E-4 mole/l respectively; the corresponding Ni ion concentration in the aqueous phase is 0.16, 0.98E-4 and 0.13E-7 mole/l respectively.

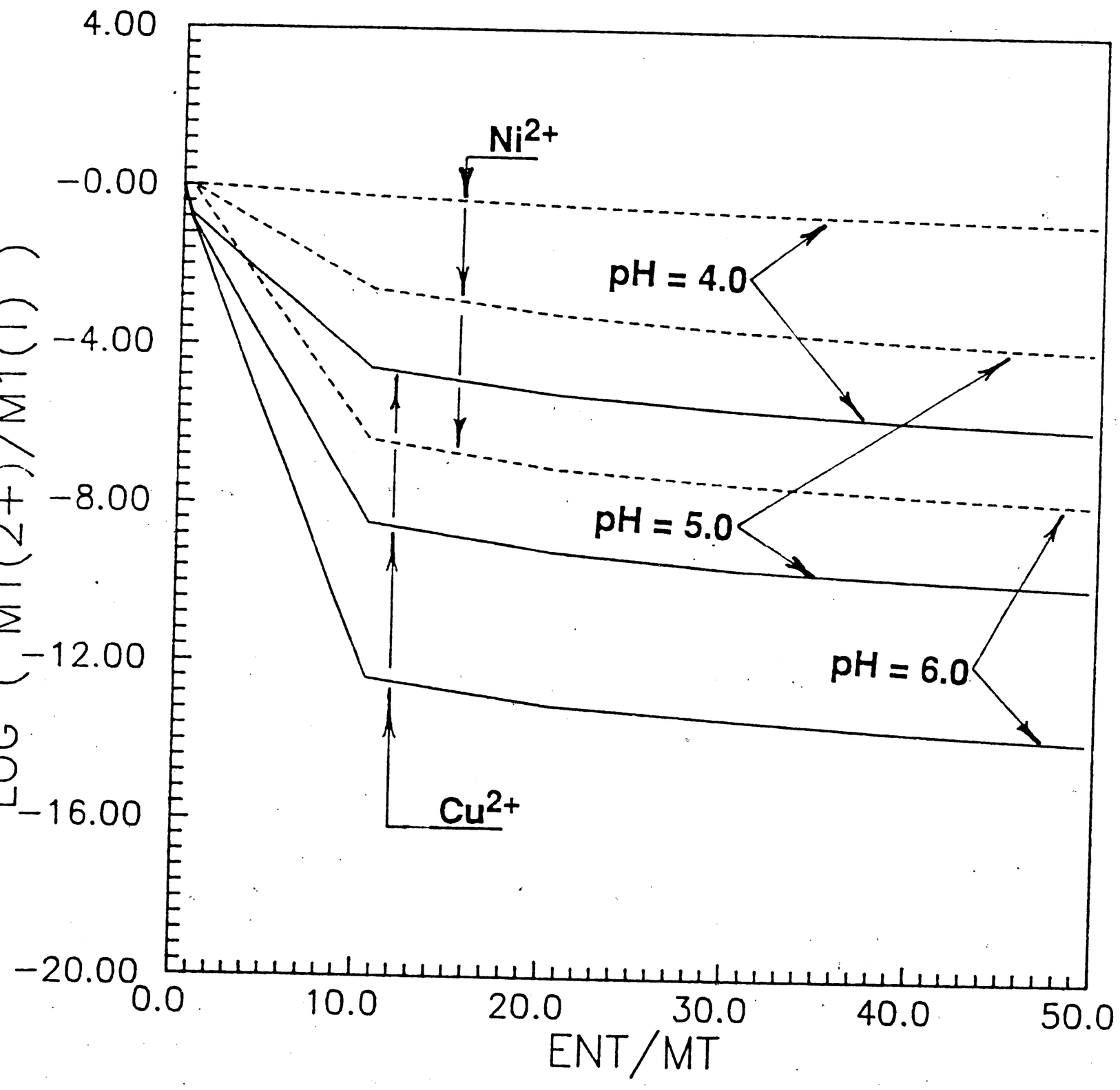


Figure 4-7: Effect of En and pH on a Binary System Containing 1 mole/l each of Nickel(II) and Copper(II)

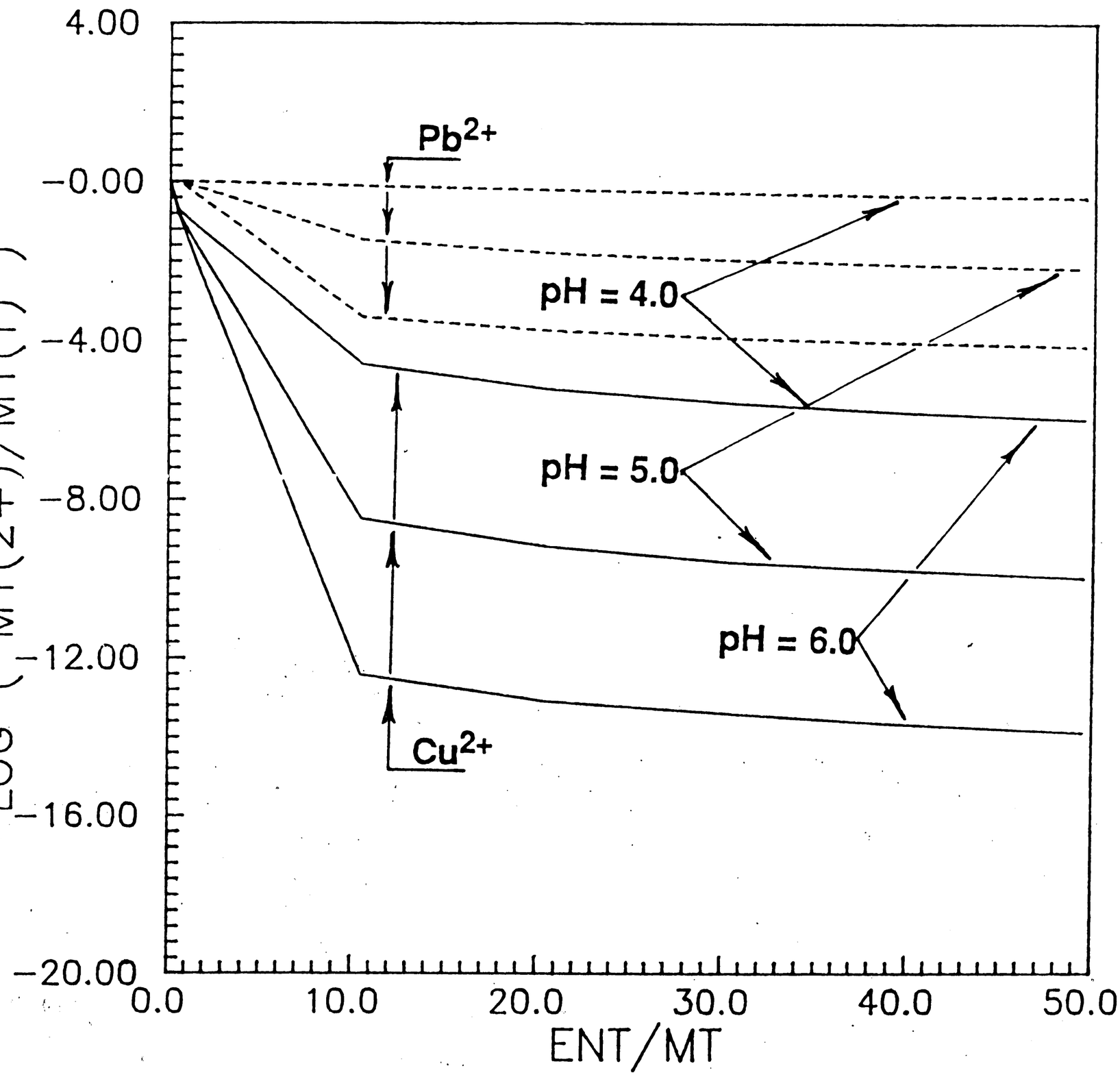


Figure 4-8: Effect of pH and En on a Binary System Containing 1 mole/l each of Lead(II) and Copper(II)

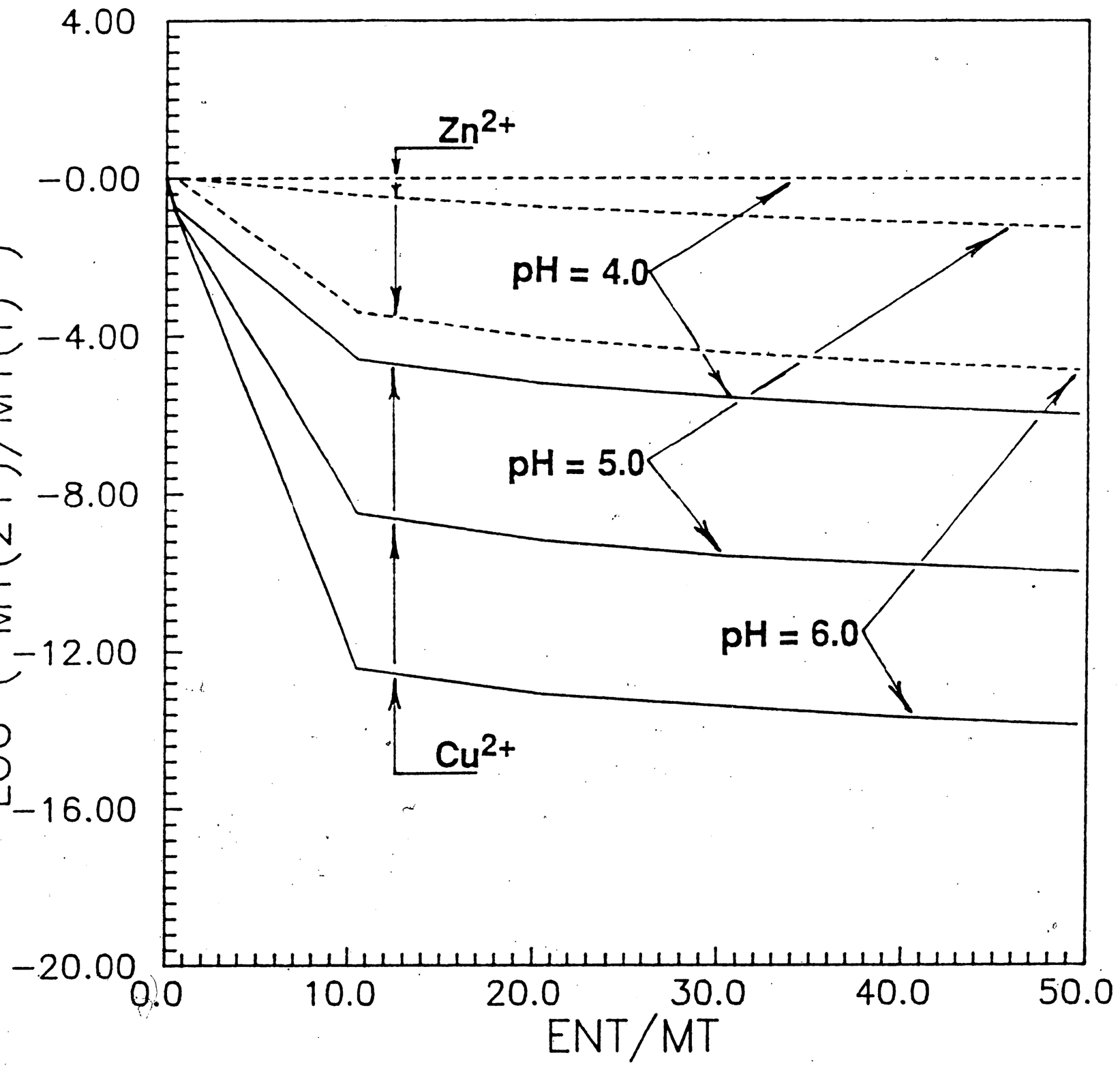


Figure 4-9: Effect of pH and En on a Binary System containing 1 mole/l each of Zinc(II) and Copper(II)

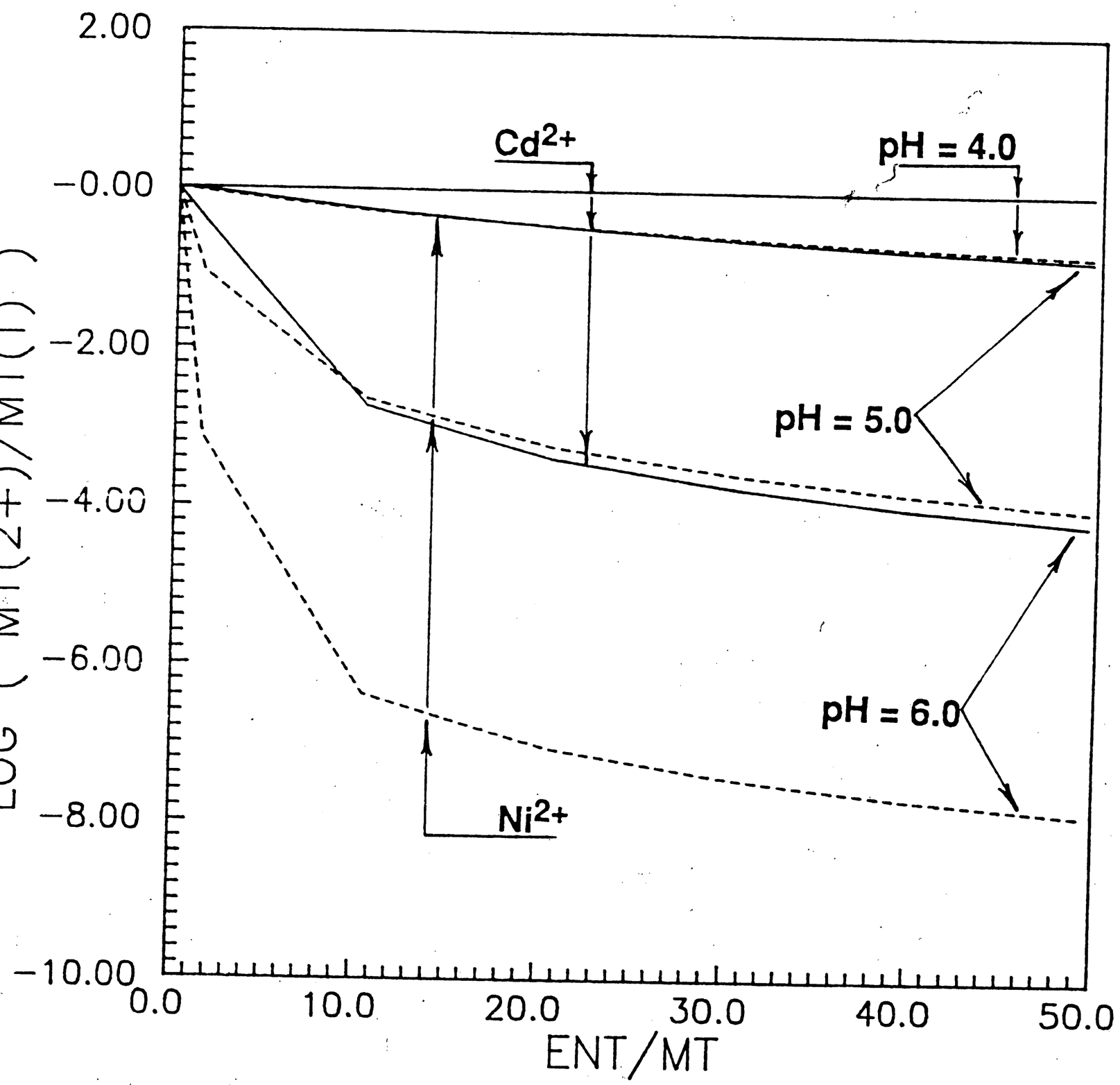


Figure 4-10: Effect of pH and En on a Binary System Containing 1 mole/l each of Cadmium(II) and Nickel(II)

4.2.7.6 Cd - Pb - En System

The concentration diagram of Pb and Cd ion as a function of pH and En is given in Fig. 4-11. At a total En concentration of 99 mole/l, the Pb ion concentration is 0.38, 0.63E-2 and 0.68E-4 mole/l at pH 4.0, 5.0 and 6.0 respectively. The corresponding Cd ion concentration is 0.96, 0.14 and 0.63E-4 mole/l respectively.

4.2.7.7 Cd - Zn - En System

The concentration of Cd and Zn ion at different pH and En concentration is plotted in Fig. 4-12. With a total En concentration of 99 mole/l and at pH of 4.0, 5.0 and 6.0, the Cd ion concentration is 0.96, 0.14 and 0.64E-4 mole/l respectively. The corresponding Zn ion concentration is 0.92, 0.053 and 0.13E-4 mole/l respectively.

4.2.7.8 Ni - Pb - En System

Fig. 4-13 describes the effect of pH and En concentration on the Ni and Pb ions for this type of binary system. At a pH of 4.0 with a total En concentration of 99 mole/l, the Ni and Pb ion concentration are 0.16 and 0.38 mole/l respectively. With the same En concentration at pH 5.0 the Ni ion concentration is 0.98E-4 mole/l with corresponding Pb ion concentration of 0.63E-2 mole/l. Increasing the pH to 6.0, the Ni and Pb ion concentration drops to 0.13E-7 and 0.69E-4 mole/l respectively.

4.2.7.9 Ni - Zn - En System

Fig. 4-14 illustrates the effect of En concentration and pH for a binary system containing Ni and Zn ions. At a total En concentration of 99 mole/l and at a pH of 4.0, 5.0 and 6.0 the Ni ion concentration is 0.16, 0.99E-4 and 0.13E-7 mole/l respectively. The corresponding Zn ion concentration is 0.92, 0.54E-1 and 0.13E-4 mole/l respectively.

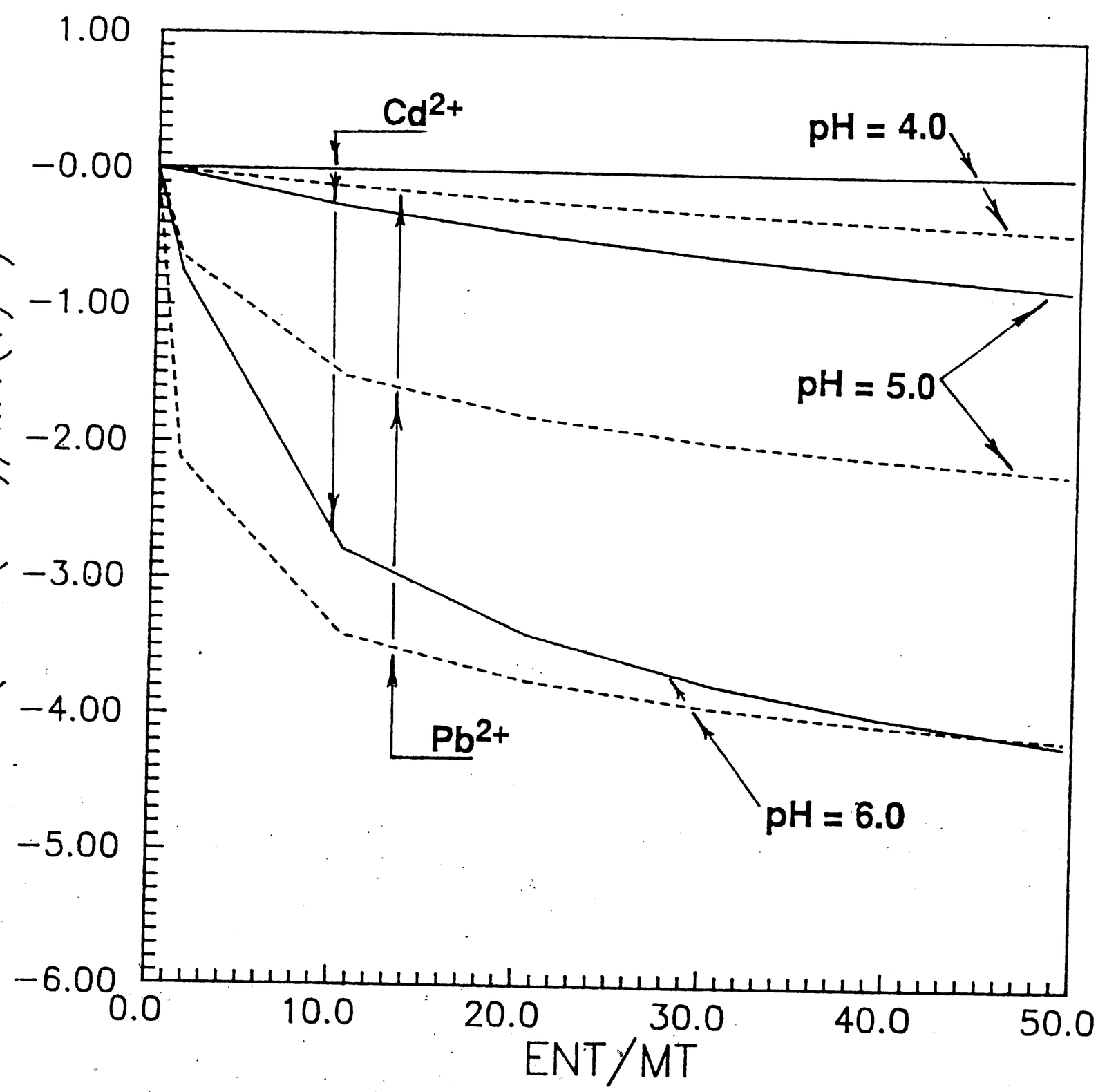


Figure 4-11: Effect of En and pH on a Binary System Containing 1 mole/l each of Cadmium(II) and Lead(II)

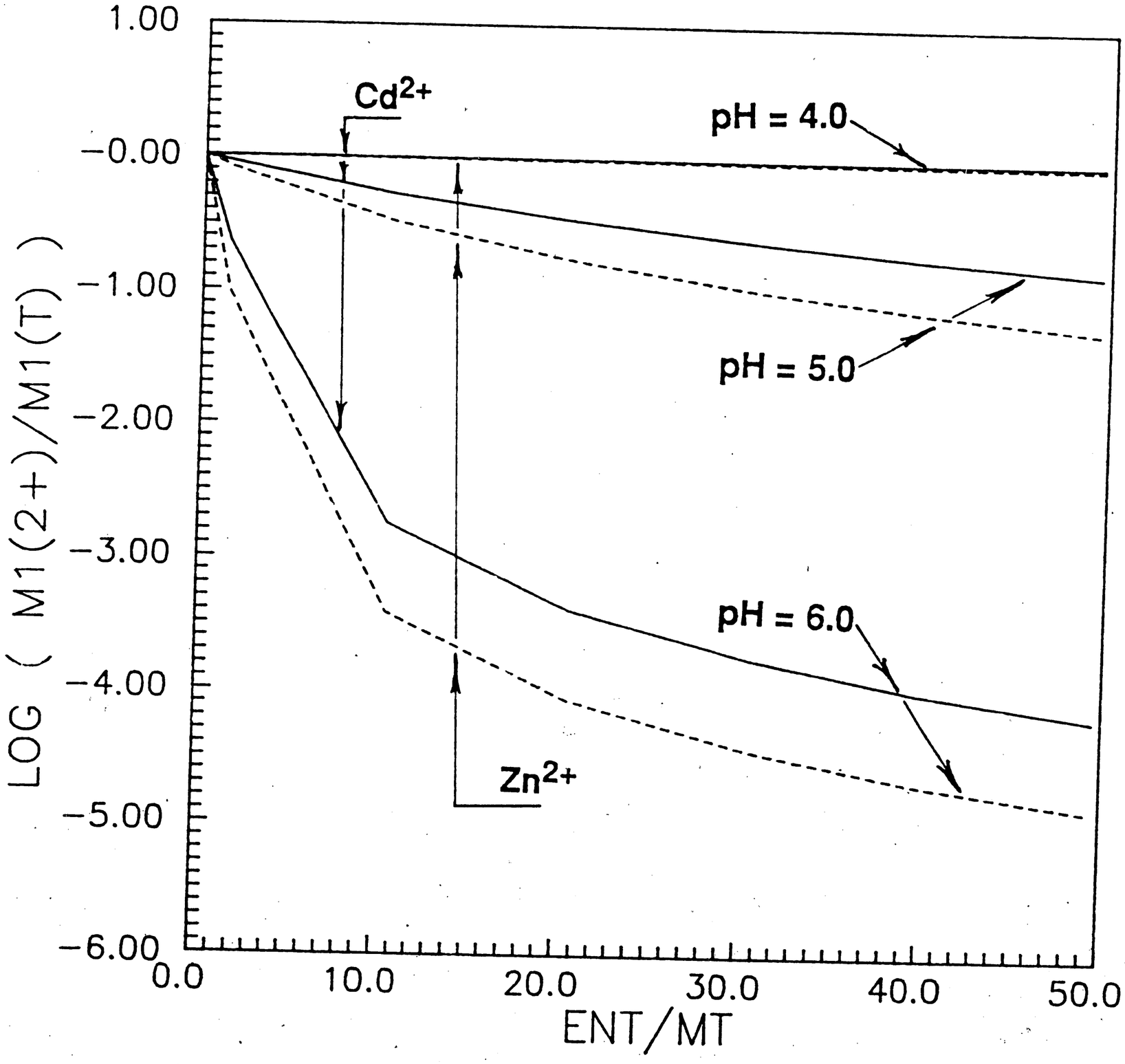


Figure 4-12: Effect of pH and En on a Binary System containing 1 mole/l each of Cadmium(II) and Zinc(II)

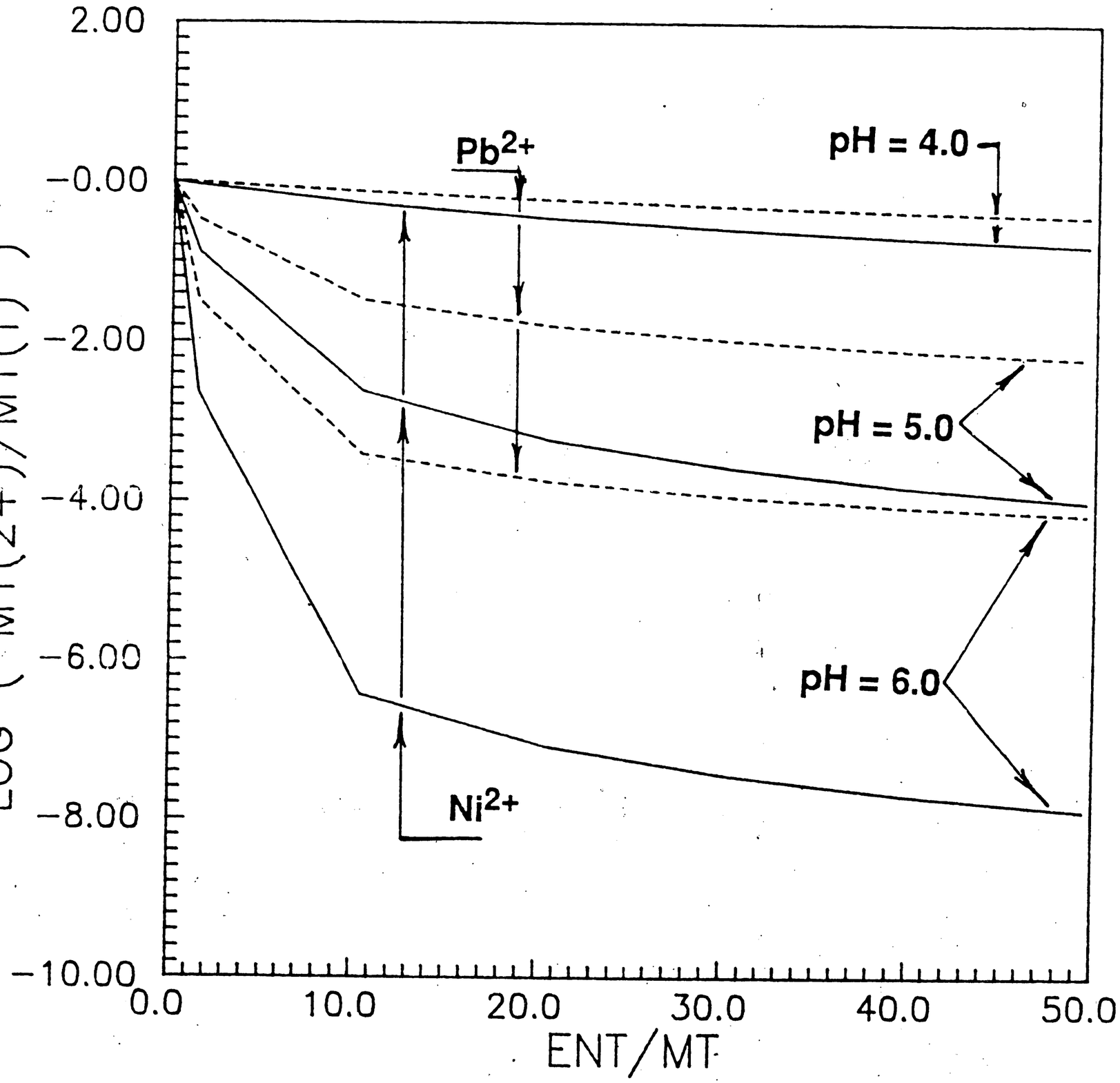


Figure 4-13: Effect of pH and En on a Binary System Containing 1 mole/l each of Nickel(II) and Lead(II)

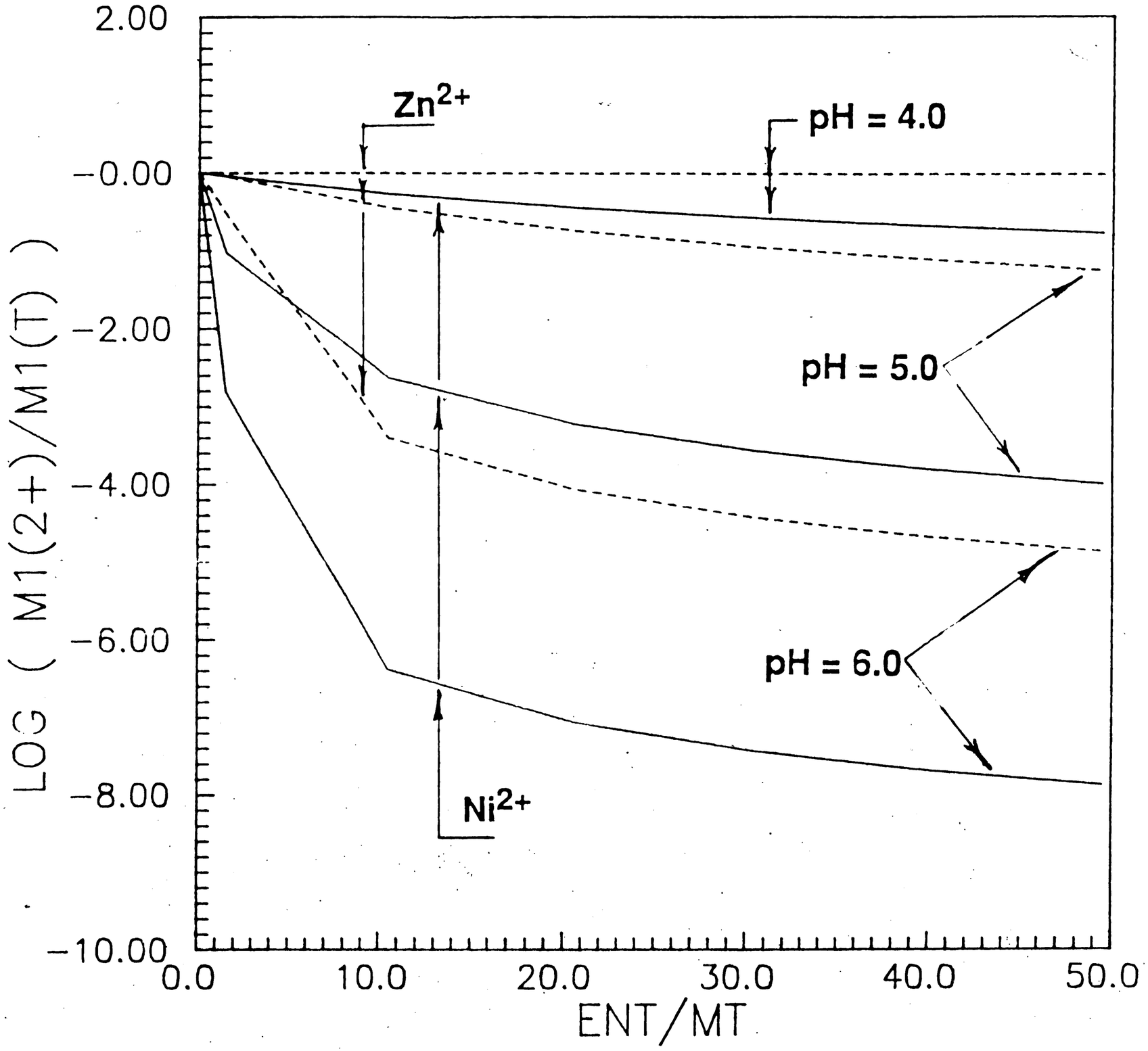


Figure 4-14: Effect of pH and En on a Binary System Containing 1 mole/l each of Nickel(II) and Zinc(II)

4.2.7.10 Pb - Zn - En System

The effect of En concentration and pH on the aqueous phase distribution of Pb and Zn ion is illustrated in Fig. 4-15. At a total En concentration of 99 mole/l and a system pH of 4.0, the Pb and Zn ion concentration are 0.92 and 0.38 mole/l respectively. With the same En concentration at pH 5.0, the Zn ion concentration is 0.53E-1 mole/l with corresponding Pb ion concentration of 0.63E-2 mole/l. An increase in pH upto 6.0 results in a Zn ion concentration of 0.13E-4 mole/l and Pb ion concentration of 0.69E-4 mole/l.

4.2.8 Effect of pH, En and Metal Concentration on the Coordination Reaction

From the above it is observed that both the pH and the En concentration plays an important role in the coordination reaction between metal and En. The stronger the stability constant of the reaction, more readily the coordinated complex formed. Due to the highest stability constant, copper undergoes the coordinated complex formation with En more easily than the other metals studied. In contrast, lead-En complexation is least favored due to the weakest stability constant among the five metals studied. However, the complexation formation of the weaker coordinated complex can be improved, at a certain En concentration, by increasing the aqueous phase pH.

Subsequent to the above, the effect of the metal ion concentration on the complexation formation at a given pH and En concentration is studied. Lead and Copper are chosen for this study because of their widest difference in the stability constant with En among the five metals. Figure 4-16 shows the effect on the metal-En complexation reaction at a copper (0.2 mole/l) to lead (1.8 mole/l) mole ratio of 1:9 at a given pH. At pH 4.0 with a total En concentration of 99 mole/l, the lead and copper concentration is 0.69 and 0.192E-6 mole/l

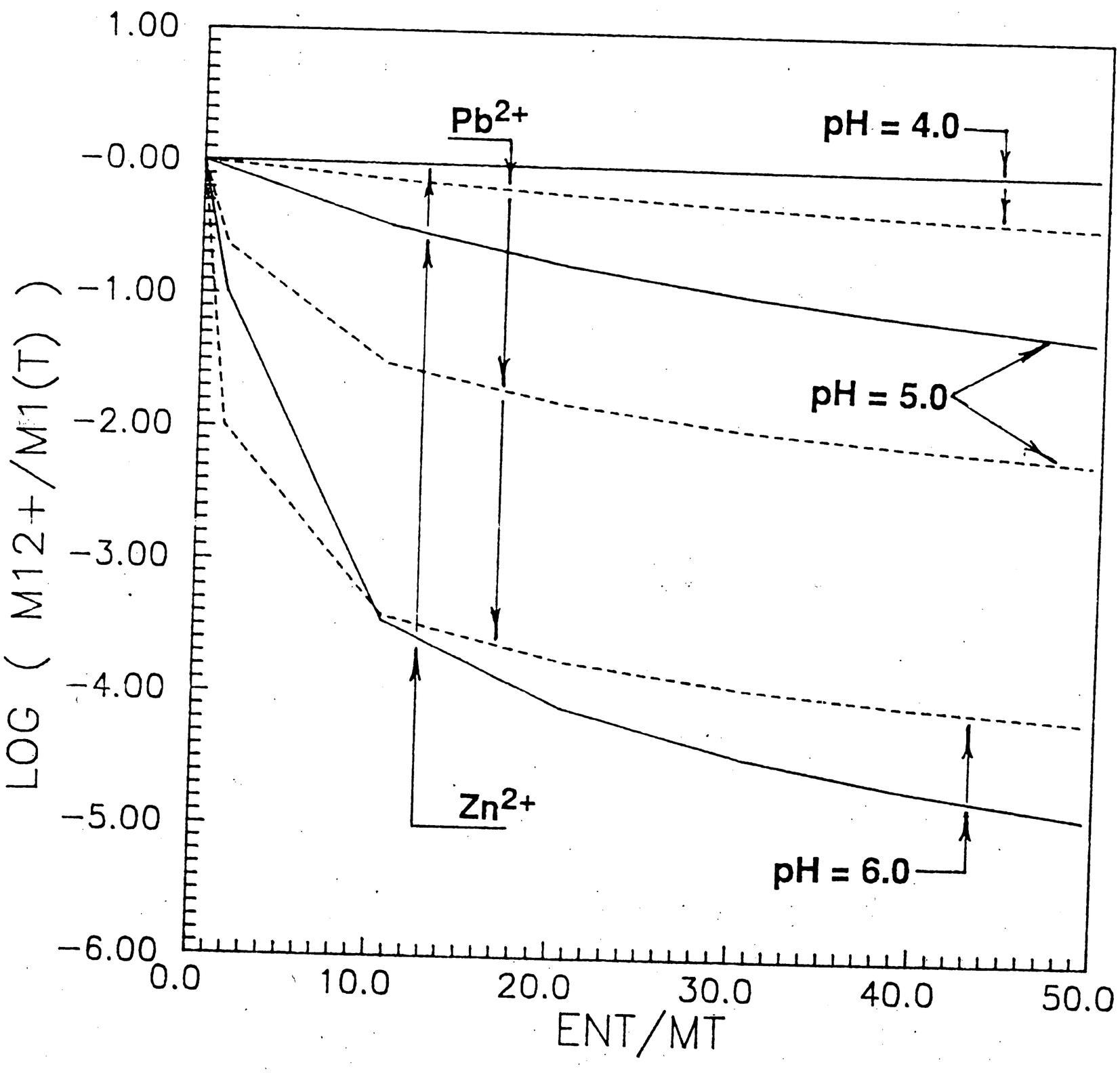


Figure 4-15: Effect of pH and En on a Binary System Containing 1 mole/l each of Lead(II) and Zinc(II)

respectively. At the same En concentration at pH 5.0, lead and copper ion concentration drops to 0.118E-1 and 0.218E-10 mole/l respectively. With a total En concentration of 99 mole/l, the lead and copper concentration further reduces to 0.12E-2 and 0.254E-14 mole/l respectively at pH 6.0. Thus, an increase of the lead concentratioin in the aqueous phase, complexation reaction, in the favour of lead, has increased by approximately seven fold over the system shown in Fig. 4-8. Figure 4-17 shows the effect of competiting metal ion concentration on the complexation reaction for a system containing copper (1.8 mole/l) to lead (0.2 mole/l) mole ratio of 9:1. For this system, at pH 4.0, 5.0 and 6.0 the copper concentration is 0.18E-5, 0.19E-9 and 0.24E-13 mole/l respectively at a total En concentration of 99 mole/l with a corresponding lead concentration of 0.78E-1, 0.13E-2 and 0.14E-4 mole/l.

A significant effect on the coordinated complex formation is observed when the aqueous phase concentration of the competiting metal ion is in the mg/l level. Figure 4-18 shows the effect of pH and En concentration on a binary system with a lead and copper concentration of 1.E-4 mole/l each (corresponding copper concentration is 6.35 mg/l). At a total En concentration of 99 mole/l, at pH 4.0, the aqueous phase copper and lead concentration is 0.65E-4 and 0.99E-4 mole/l respectively. Thus the copper concentration is reduced by about 35% at pH 4.0 while lead concentration remains practically unaffected at pH 4.0. However, copper forms strong complexes as the system pH is increased; at pH 5.0 and 6.0 the copper concentration is 0.66E-6 and 0.13E-9 mole/l respectively at a total En concentration of 99 mole/l, the corresponding lead concentration being 0.98E-4 and 0.42E-4 mole/l.

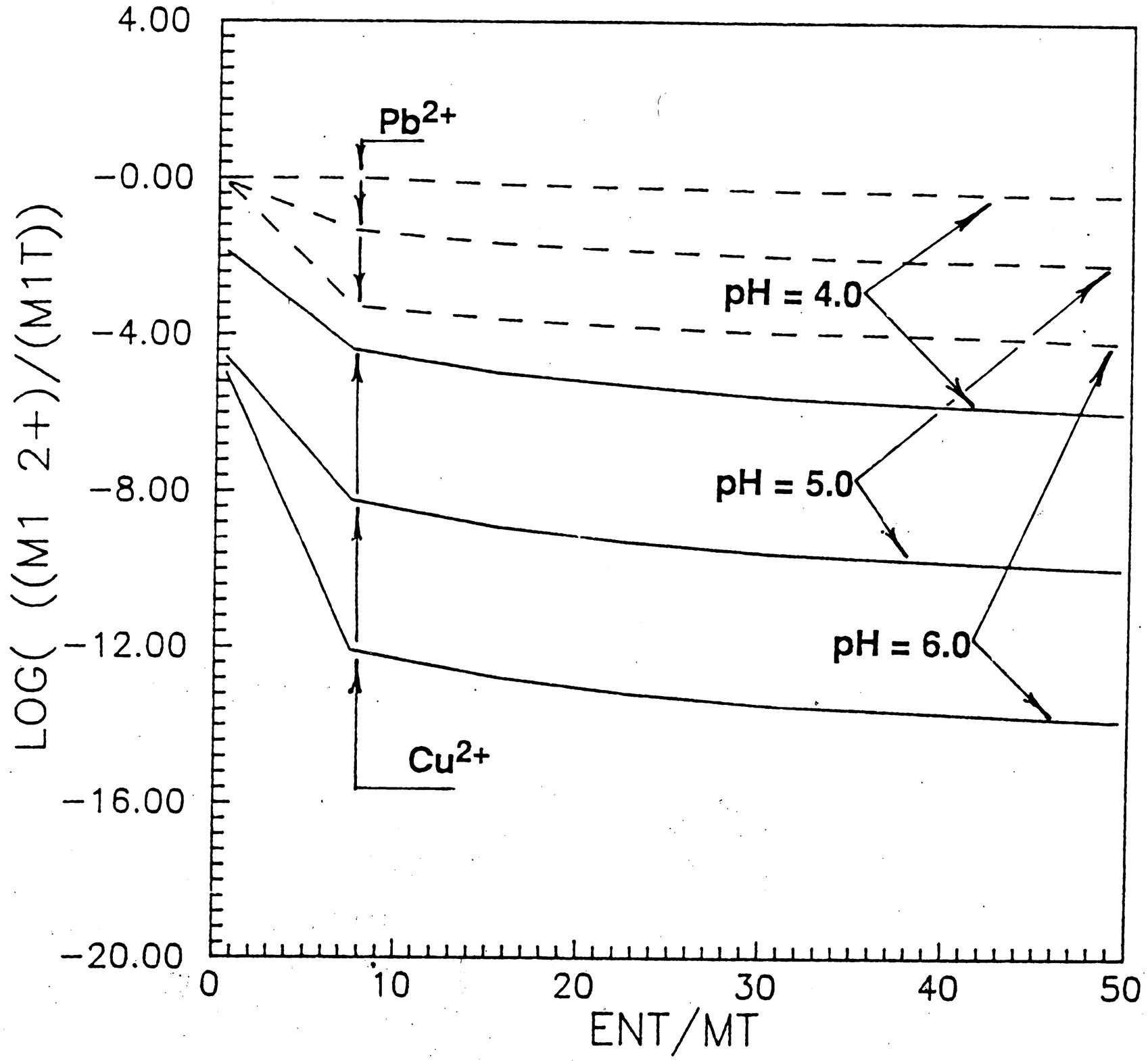


Figure 4-16: Effect of pH and En Concentration on a Binary System with 0.2 mole/l Copper(II) and 1.8 mole/l Lead(II)

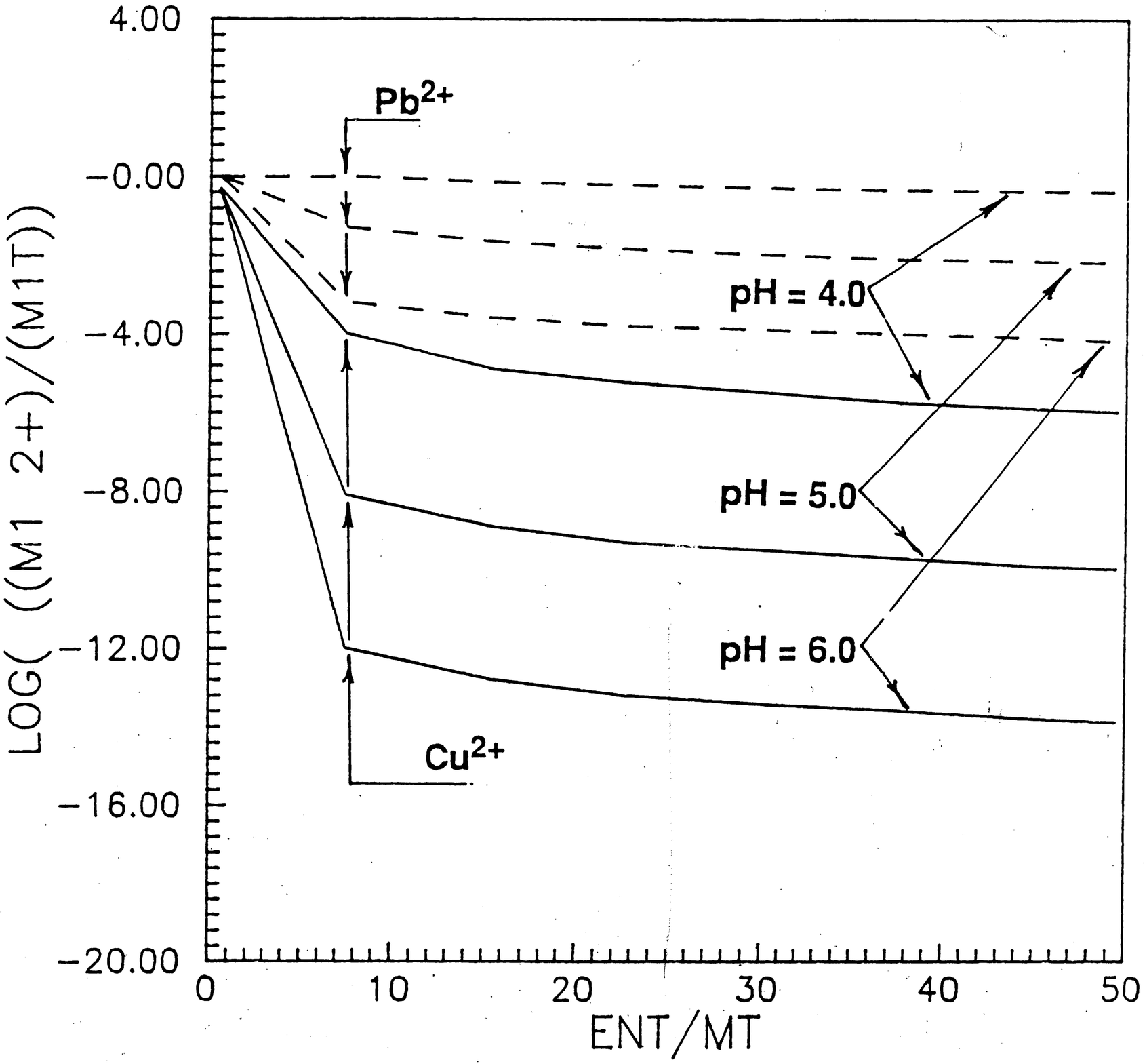


Figure 4-17: Effect of pH and En Concentration on a Binary System with 1.8 mole/l Copper(II) and 0.2 mole/l Lead(II)

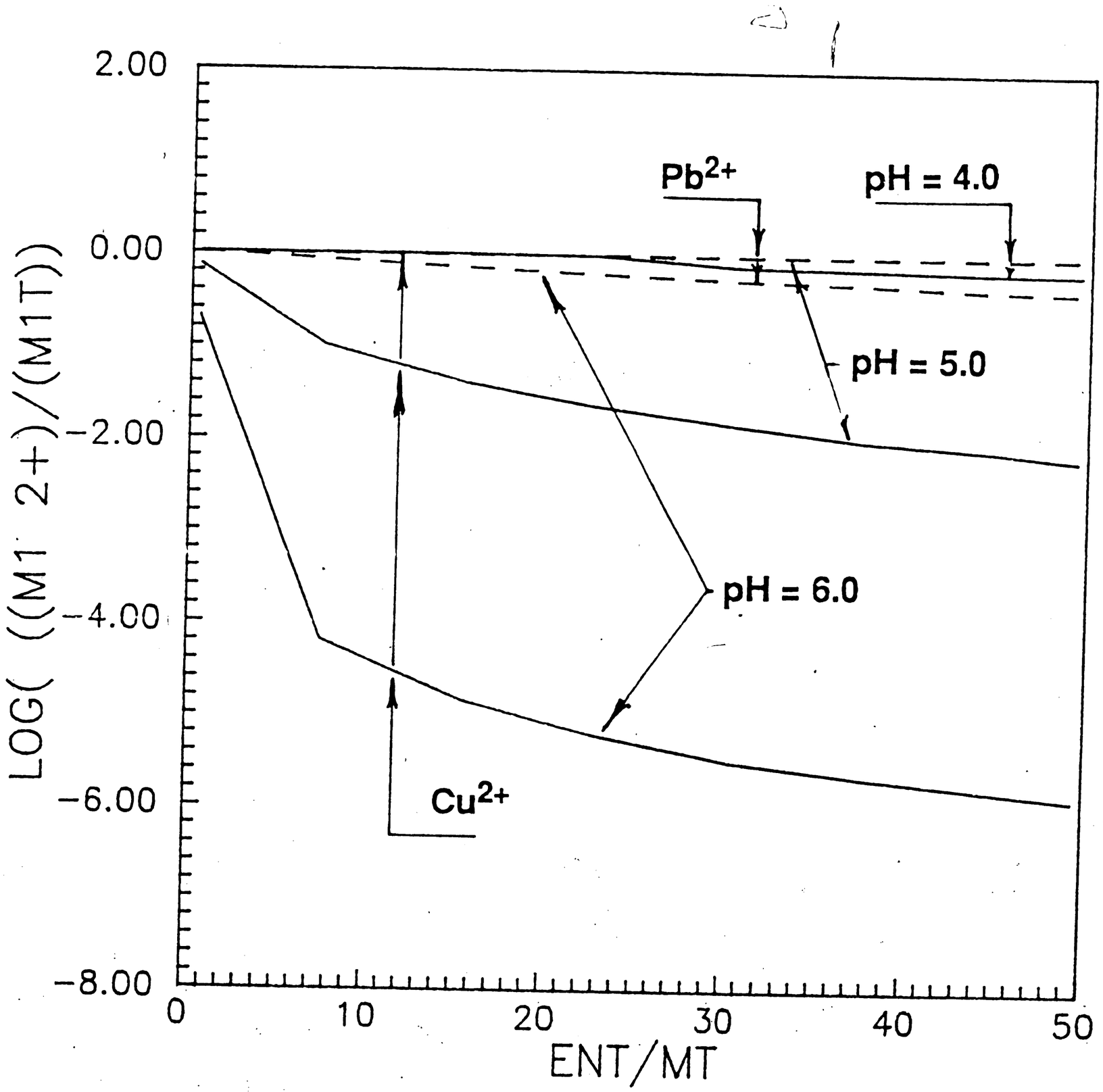


Figure 4-18: Effect of pH and En Concentration Binary System with 1.E-4 mole/l of Copper(II) and Lead(II)

4.3 MODIFYING METAL SELECTIVITY OF RESIN : EXPERIMENTAL STUDY

4.3.1 Column Experiment with DP-1 Resin at pH 4.0

The effluent history of the column experiment with DP-1 resin at pH 4.0 is presented in Fig. 4-19 and Fig. 4-20. From Fig. 4-19, an enlarged view of the column experiment upto 100 BV, it is observed that the breakthrough of nickel, being the least preferred species by carboxylate resin, occurs within 2 bed volume (BV) of the column experiment. Zinc, cadmium and copper breakthrough occurs one after the other in line with the selectivity series given in Chapter 2. From Fig. 4-20 it is seen that that the breakthrough for lead, being the most preferred species of carboxylate resin, occurs at 750 BV, well after the breakthrough of remaining metals. The metal ion separation factor, observed from this column run by regenerating the column, is given in Table 4-1.

From the above column study, the relative position of the metals in the decreasing order of separation factor or selectivity series, remains unaltered as seen in Chapter 2. However, the breakthrough of lead from the column is diffused although lead is the most selective species.

4.3.2 Column Study with DP-1 Resin at pH 4.0 alongwith En

The effluent breakthrough from column study with DP-1 resin at pH 4.0 incorporating the ligand En is presented in Fig. 4-21. Fig. 4-22 is an enlarged view of the effluent history upto 120 BV. The En concentration was about 53 times the total molal concentration of copper. These effluent histories are analogous to the system without any ligand and En has no effect on the metal ion breakthrough. The metal ion separation factor of the resin for this column run is presented in Table 4-2 and it is observed that the metal ion separation factors remain practically unaltered.

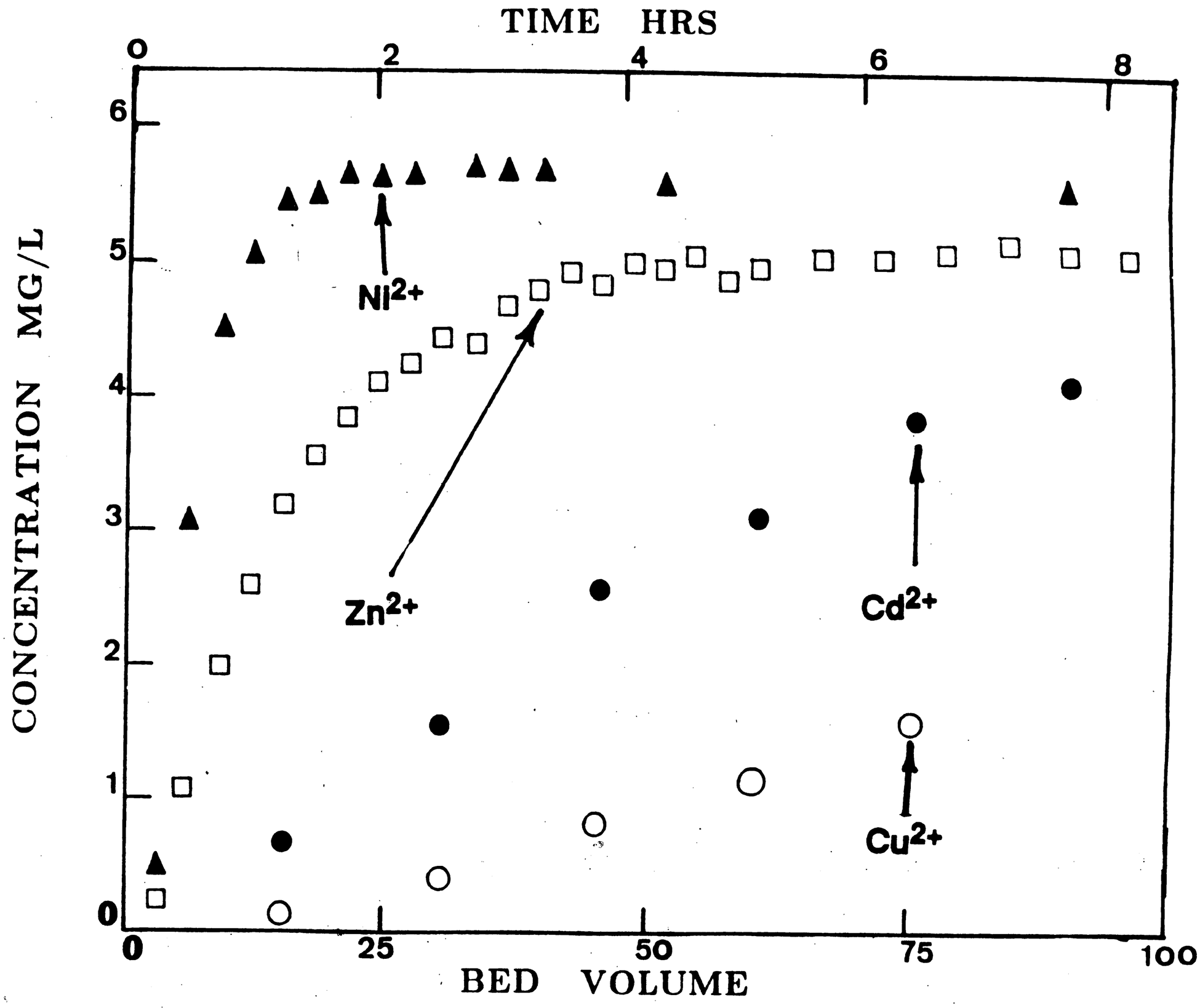


Figure 4-19: Effluent History of DP-1 Resin at pH 4.0 (upto 100 BV)

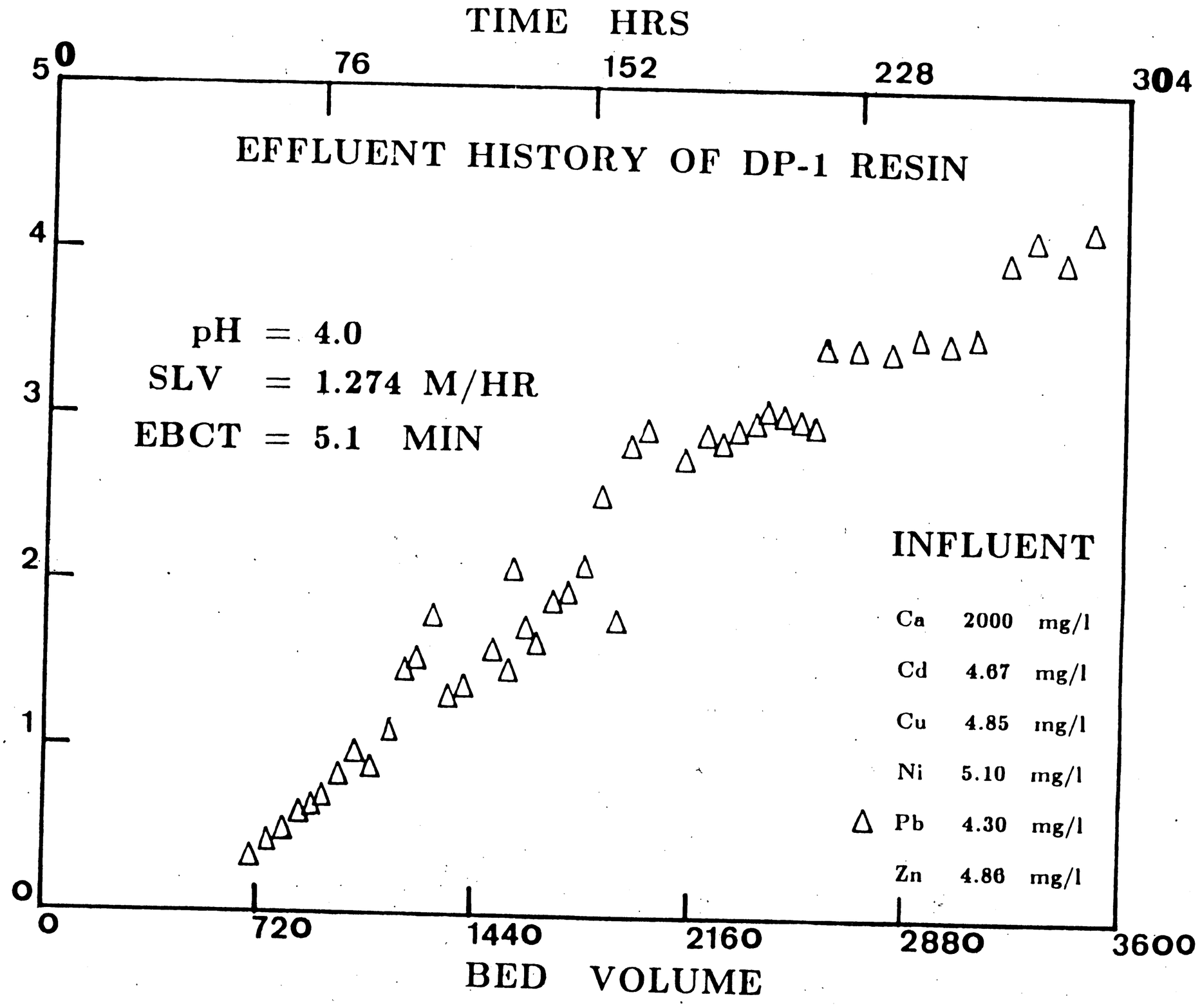


Figure 4-20: Effluent History of Lead from the Column Study with DP-1 Resin at pH 4.0

Table 4-1: Metal Ion Separation Factor from the Column Experiment with DP-1 Resin at pH 4.0

OPERATING PH OF THE COLUMN RUN = 4.0

WT. OF RESIN TAKEN (GM.) = 5.0013

RESIN REGENERATION VOL, (LIT.) = .20

COUNTER ION	AQUEOUS PHASE CONCENTRATION (MG/L)	(MEQ./L)	RES.PHASE CONC. (MG/L)	RES.PHASE MASS (MEQ)	AQ.PHASE FRACN.	RES.PHASE FRACN.	SELECTIVITY	SEPARATION FACTOR ALPHA(ME2+/CA)
CA2+	.200E+04	.100E+03	.222E+03	.222E+01	.994E+00	.674E+00	.68	1.00
CO2+	.467E+01	.830E-01	.917E+01	.326E-01	.825E-03	.988E-02	11.97	17.67
CU2+	.485E+01	.153E+00	.378E+02	.238E+00	.152E-02	.722E-01	47.61	70.25
NI2+	.510E+01	.174E+00	.732E+00	.499E-02	.173E-02	.151E-02	.88	1.29
PB2+	.430E+01	.415E-01	.408E+03	.787E+00	.413E-03	.239E+00	578.24	853.17
ZN2+	.486E+01	.149E+00	.223E+01	.136E-01	.148E-02	.413E-02	2.79	4.12

CAPACITY OF THE RESIN AT THE OPERATING CONDITION (IN MEQ/GM) = .660

4.3.3 Study for the Failure of the Column Study with En

From the previous theoretical calculations it is observed that at pH 4.0 and with a low aqueous phase concentration of metal ion, the most complex forming metal, copper, was unable to undergo coordination reaction with En completely. As a verification of this theoretical prediction, a solution containing copper was titrated with En at pH 4.0. Fig. 4-23 is the titration curve of a solution with 1000 mg/l original copper concentration with a background sodium nitrate concentration of 0.11 M. From this Figure it is observed that approximately 50% of the copper present in the solution has undergone complexation reaction at a total En to total copper ratio of 10.0. This experimental data matches with the theoretical prediction, for this titration system, for a pH of 3.9. The theoretical prediction at pH 4.0 for this system is also superimposed.

The titration curve of copper(II) with En at pH 4.0 with an original copper concentration of 100 mg/l and a sodium nitrate concentration of 0.11 M is presented in Fig. 4-24 along with the theoretical prediction for this system at pH 3.9 and 4.0. The free copper concentration is observed to be 50% of the total even with a total En to total copper ratio of 60.0. The calculations for these experimental titration curves are given in Appendix W and Appendix X respectively.

The above two titration experiments indicate that at pH 4.0 with a low aqueous phase copper concentration, the coordinated complex forming ability of En is poor. The theoretical predictions (for calculations ref. Appendix Y) also are in good match with the experimental data and thus testify that the stability constant data considered for the theoretical calculations in the previous section are valid and all calculations hold good for prediction. The theoretical calculation for the column experiment with En is performed (ref. Table 4-3) and

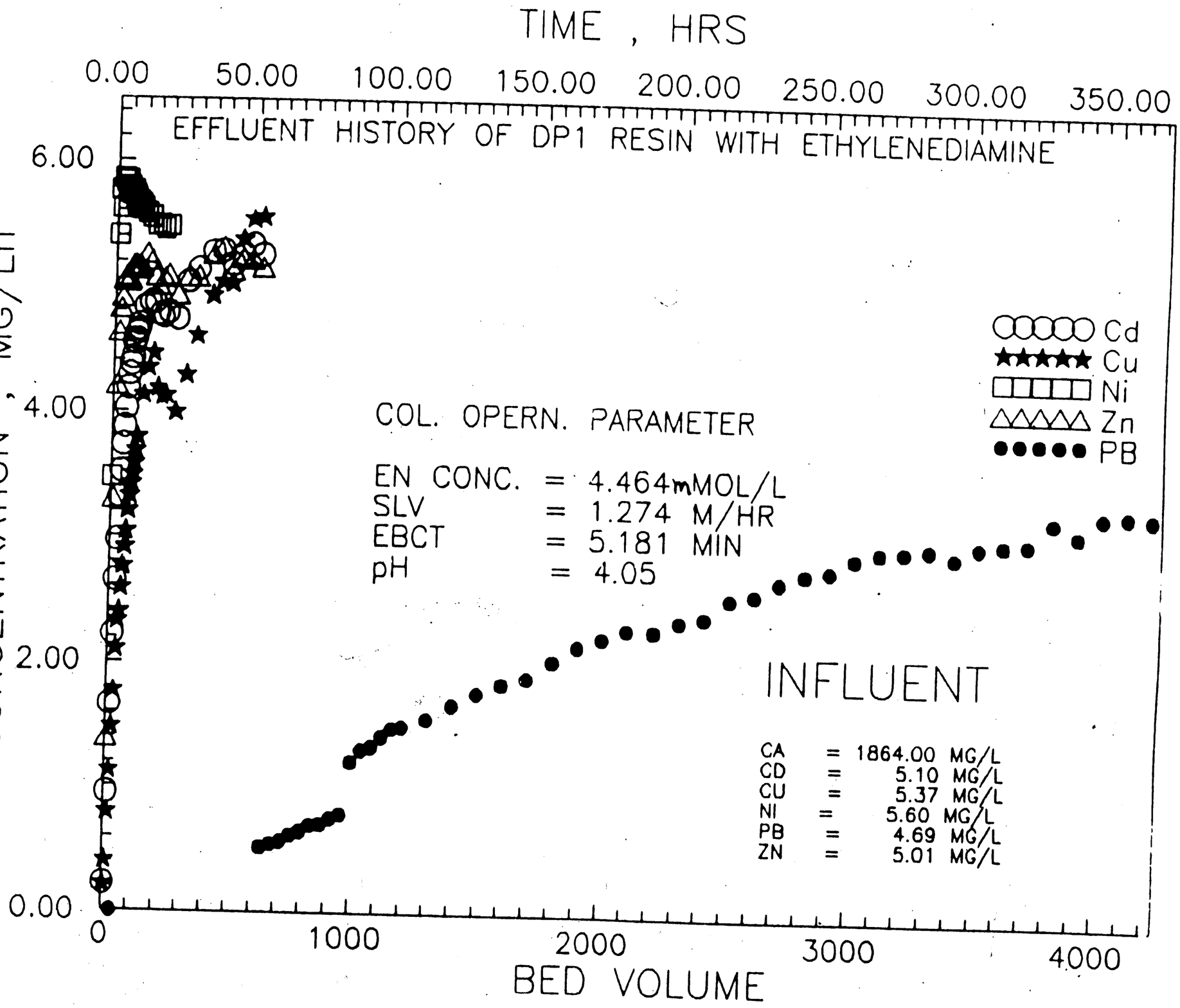


Figure 4-21: Effluent History of DP-1 Resin at pH 4.0 with EN

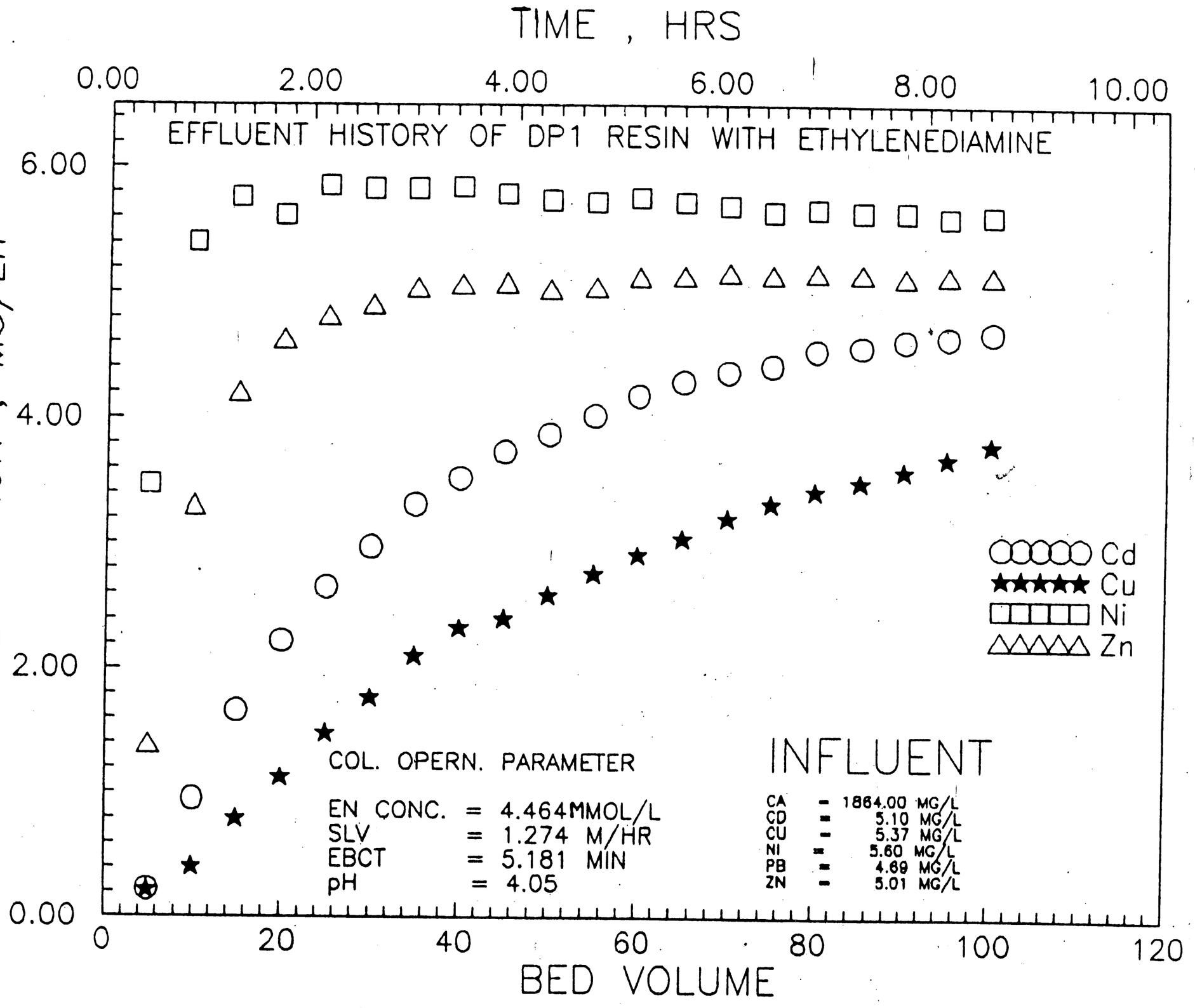


Figure 4-22: Effluent History of DP-1 Resin at pH 4.0 with EN (upto 120 BV)

Table 4-2: Metal Ion Separation Factors from the Column Study of DP-1 Resin at pH 4.0 with En

EN CONCENTRATION =APPROX. 60 MOLAL TIMES OF CU++ = 4.464 mmol/l.

OPERATING PH OF THE COLUMN RUN = 4.0

WT. OF RESIN TAKEN (GM.) = 5.0008

RESIN REGENERATION VOL, (LIT.) = .20

COUNTER ION	AQUEOUS PHASE CONCENTRATION (MG/L)	(MEQ./L)	RES.PHASE CONC. (MG/L)	RES.PHASE MASS (MEQ)	AQ.PHASE FRACN.	RES.PHASE FRACN.	SELECTIVITY	SEPARATION FACTOR ALPHA(ME2+/CA)
CA2+	.185E+04	.932E+02	.226E+03	.226E+01	.993E+00	.586E+00	.59	1.00
CO2+	.510E+01	.907E-01	.145E+02	.515E-01	.967E-03	.133E-01	13.79	23.38
CU2+	.537E+01	.169E+00	.525E+02	.330E+00	.180E-02	.856E-01	47.51	80.55
NI2+	.560E+01	.191E+00	.900E+00	.613E-02	.203E-02	.159E-02	.78	1.32
PB2+	.469E+01	.453E-01	.619E+03	.120E+01	.482E-03	.310E+00	641.97	1088.37
ZN2+	.501E+01	.153E+00	.260E+01	.159E-01	.163E-02	.412E-02	2.52	4.27

CAPACITY OF THE RESIN AT THE OPERATING CONDITION (IN MEQ/GM) = .772

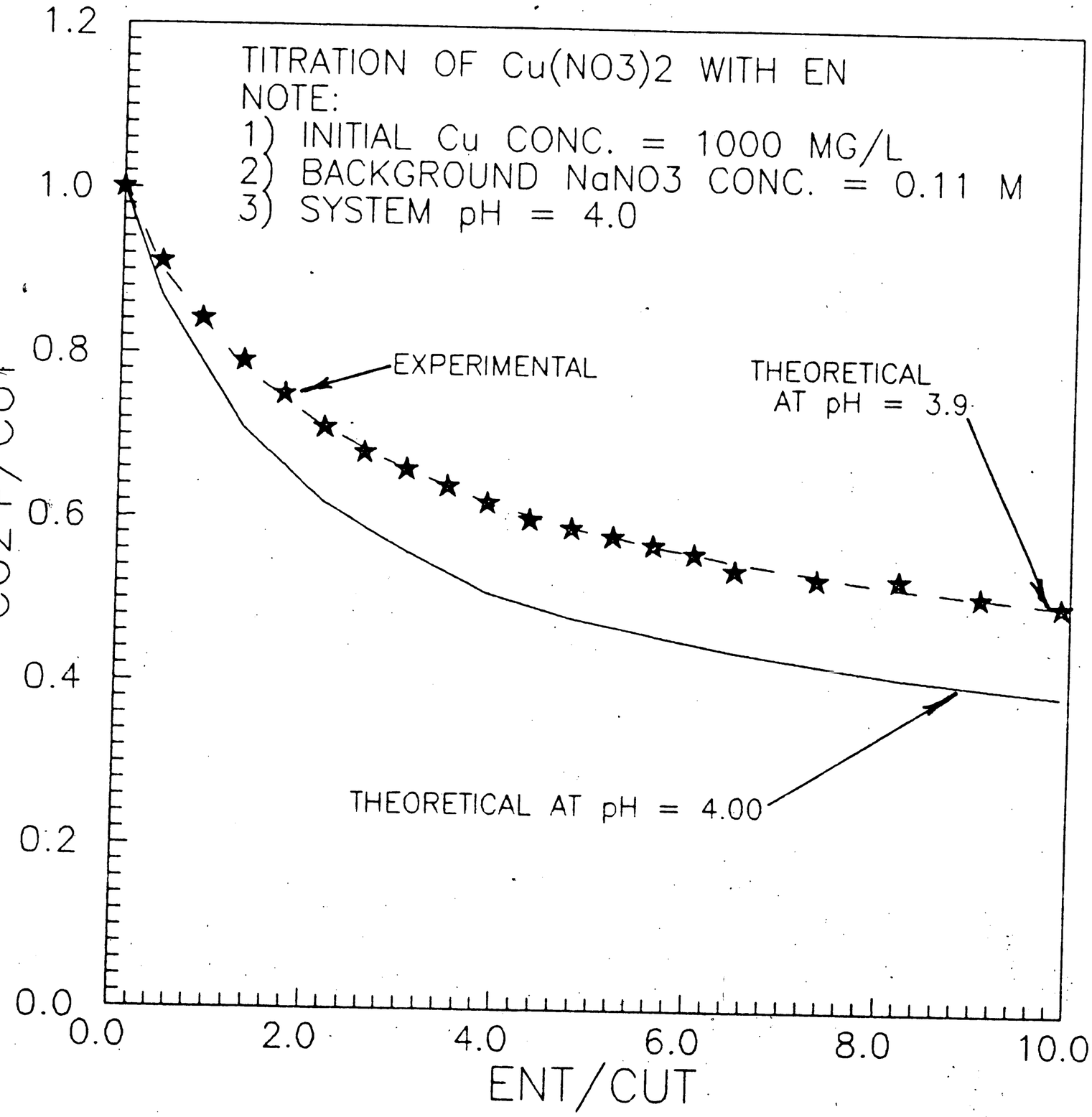


Figure 4-23: Titration of Copper(II) with En at pH 4.0 (origanl Copper Concentration = 1000 mg/l)

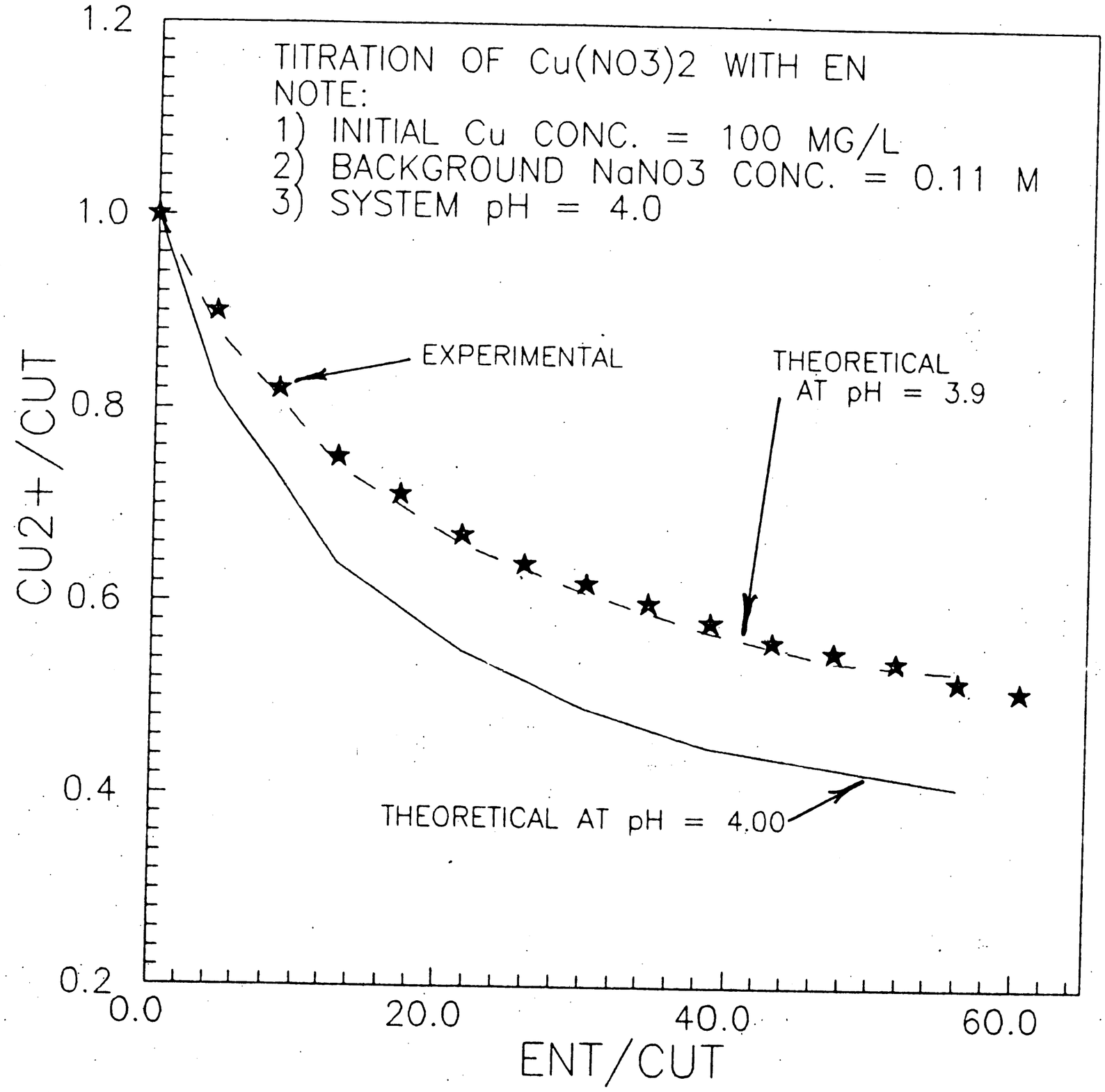


Figure 4-24: Titration of Copper(II) with En at pH 4.0 (original Copper Concentration = 100 mg/l)

it is observed that the aqueous phase free copper concentration was little affected at pH 4.0 in the presence of En. These calculations and experiments explain for the failure of the column study with En and also support the prediction that at low concentration of metals and at a low system pH, complexation of copper with En is difficult to attain.

4.3.4 Column Study with DP-1 Resin with En at pH 5.0

The effluent history of the column study with En at pH 5.0 is presented in Fig. 4-25 for the effluent upto 250 BV. The concentration of the metals in the feed for this column study was close to the previous two experiments. The empty bed contact time (EBCT) and the superficial linear velocity (SLV) for this column experiment were also close to the previous column studies. In other words, all the parameters of this column study were nearly similar to the other two column studies with two exceptions; the feed pH of this experiment is 5.05 and the En content in the feed is approximately 100 molal times the presence of all the metals (except calcium).

From Fig. 4-25 it is observed that the breakthrough of the copper occurs first from the column, well ahead of nickel, the least preferred species by the carboxylate resins. This clearly indicates that under the column operating conditions, the copper has become the least preferred species although copper ranks second, in the order of decreasing selectivity scale, of the five metals studied. Based on the influent feed composition, the theoretical study for the distribution of different metal species is presented in Table 4-4, which shows that the free copper concentration in the influent was in micro-gm/l level although the actual copper concentration in the influent is 4.65 mg/l.

The separation factor, calculated from the column regeneration, has been presented in Table 4-5 and from this table it is observed that the separation

Table 4-3: Theoretical Calculation for the Speciation of Metals with En at pH 4.0 for the Column Study with DP-1 Resin

IER = 0 PH = 4.000

EN=	.73710E-11	ENH=	.62737E-05	ENH2=	.44415E-02
CO2+ =	.45400E-04	COEN =	.84058E-10	COEN2 =	.19593E-15
CU2+ =	.68407E-04	CUEN =	.15945E-04	CUEN2 =	.14796E-06
NI2+ =	.95382E-04	NIEN =	.17660E-07	NIEN2 =	.20631E-12
PB2+ =	.22598E-04	PBEN =	.16657E-08	PBEN2 =	.38827E-13
ZN2+ =	.76600E-04	ZNEN =	.28298E-09	ZNEN2 =	.16568E-15

ENT = .00446
MT = .00032
RATIO = 13.75655

NOTE = ALL CONCENTRATIONS ARE IN MOLE/L

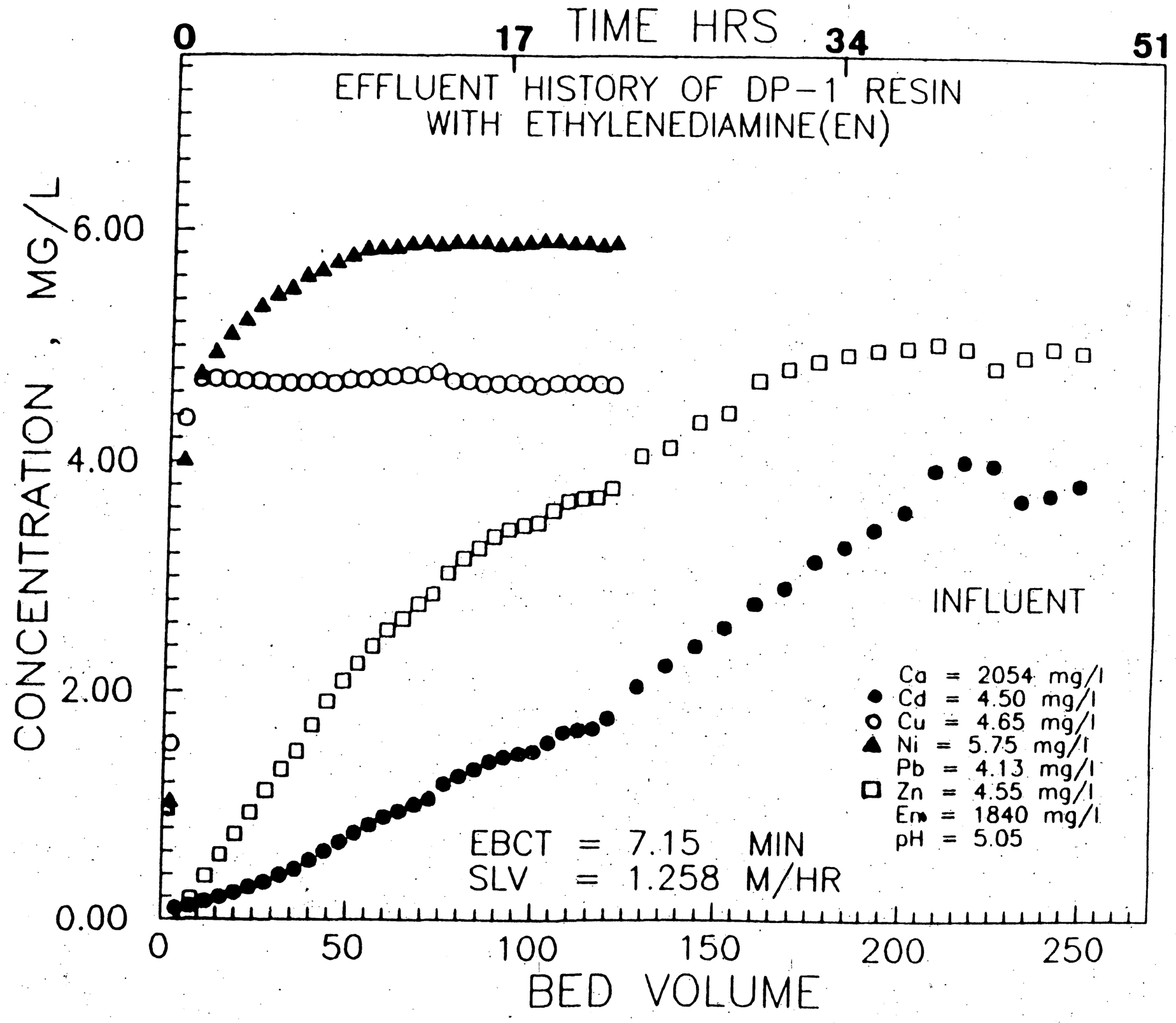


Figure 4-25: Effluent History of Column Study with En at pH 5.05

Table 4-4: Theoretical Study for the Distribution of Metal Species for the Column Study with En at pH 5.0

		IER = 0		PH = 5.000	
EN=	.49948E-08	ENH=	.42512E-03	ENH2=	.30096E-01
CO2+ =	.39950E-04	COEN =	.50122E-07	COEN2 =	.79167E-11
CU2+ =	.63534E-07	CUEN =	.10035E-04	CUEN2 =	.63101E-04
NI2+ =	.86999E-04	NIEN =	.10915E-04	NIEN2 =	.86405E-07
PB2+ =	.18953E-04	PBEN =	.94667E-06	PBEN2 =	.14952E-12
ZN2+ =	.69326E-04	ZNEN =	.17355E-06	ZNEN2 =	.68854E-10
		ENT =	.03067		
		MT =	.00030		
		RATIO =	102.02927		

NOTE = ALL CONCENTRATIONS ARE IN MOLE/L

factor of all the metals with respect to calcium has increased due to the effect of pH except for copper for which the separation factor with respect to calcium has come down to 7.23 from approximately 70 to 80 observed in the previous two column studies. Figure 4-26 is the plot for the effluent breakthrough for lead from this column study which shows that the breakthrough pattern of lead remains practically unaffected under the column operating conditions. The lead-copper separation factor has improved from about 10-12 to about 250 and the third most preferred species, cadmium, has become the second most preferred species due to the selectivity reversal effect. The cadmium-copper separation factor has reversed from 0.06 at pH 4.0 to about 20 at pH 5.0 with En. Under the column operating conditions with En, the selectivity series for the metal ions can be drawn as : lead > cadmium > zinc > nickel > copper.

4.4 OBSERVATIONS

From the foregoing theoretical calculations and column studies for the effect of pH, En and metal concentration on the coordination of metal ions the followings emerges :

- Selective complexation reaction of metal ions by a ligand depends on the difference of the stability constant data between the two metal to be separated. The greater the difference, the better will be the separation of the metals; the component with higher stability constant will undergo stronger complexation reaction with the ligand and can be separated subsequently from the weaker complexed metal by adsobing the weaker complexed metal onto ion

Table 4-5: Separation Factor of Metals from the Column Run with En at pH 5.0

EN CONCENTRATION = APPROX. 100 MOLAL TIMES OF ALL METALS

OPERATING PH OF THE COLUMN RUN = 5.0

WT. OF RESIN TAKEN (GM.) = .9980

RESIN REGENERATION VOL, (LIT.) = .25

COUNTER ION	AQUEOUS PHASE CONCENTRATION (MG/L)	(MEQ./L)	RES.PHASE CONC. (MG/L)	RES.PHASE MASS (MEQ)	AQ.PHASE FRACN.	RES.PHASE FRACN.	SELECTIVITY	SEPARATION FACTOR ALPHA(ME2+/CA)
CA2+	.205E+04	.103E+03	.666E+02	.832E+00	.994E+00	.537E+00	.54	1.00
CD2+	.450E+01	.801E-01	.229E+02	.102E+00	.775E-03	.657E-01	84.78	156.93
CU2+	.465E+01	.146E+00	.109E+01	.858E-02	.142E-02	.554E-02	3.91	7.23
NI2+	.575E+01	.196E+00	.700E+00	.596E-02	.190E-02	.385E-02	2.03	3.76
PB2+	.413E+01	.399E-01	.237E+03	.571E+00	.386E-03	.368E+00	954.82	1767.39
ZN2+	.455E+01	.139E+00	.391E+01	.299E-01	.135E-02	.193E-01	14.33	26.52

CAPACITY OF THE RESIN AT THE OPERATING CONDITION (IN MEQ/GM) = 1.552

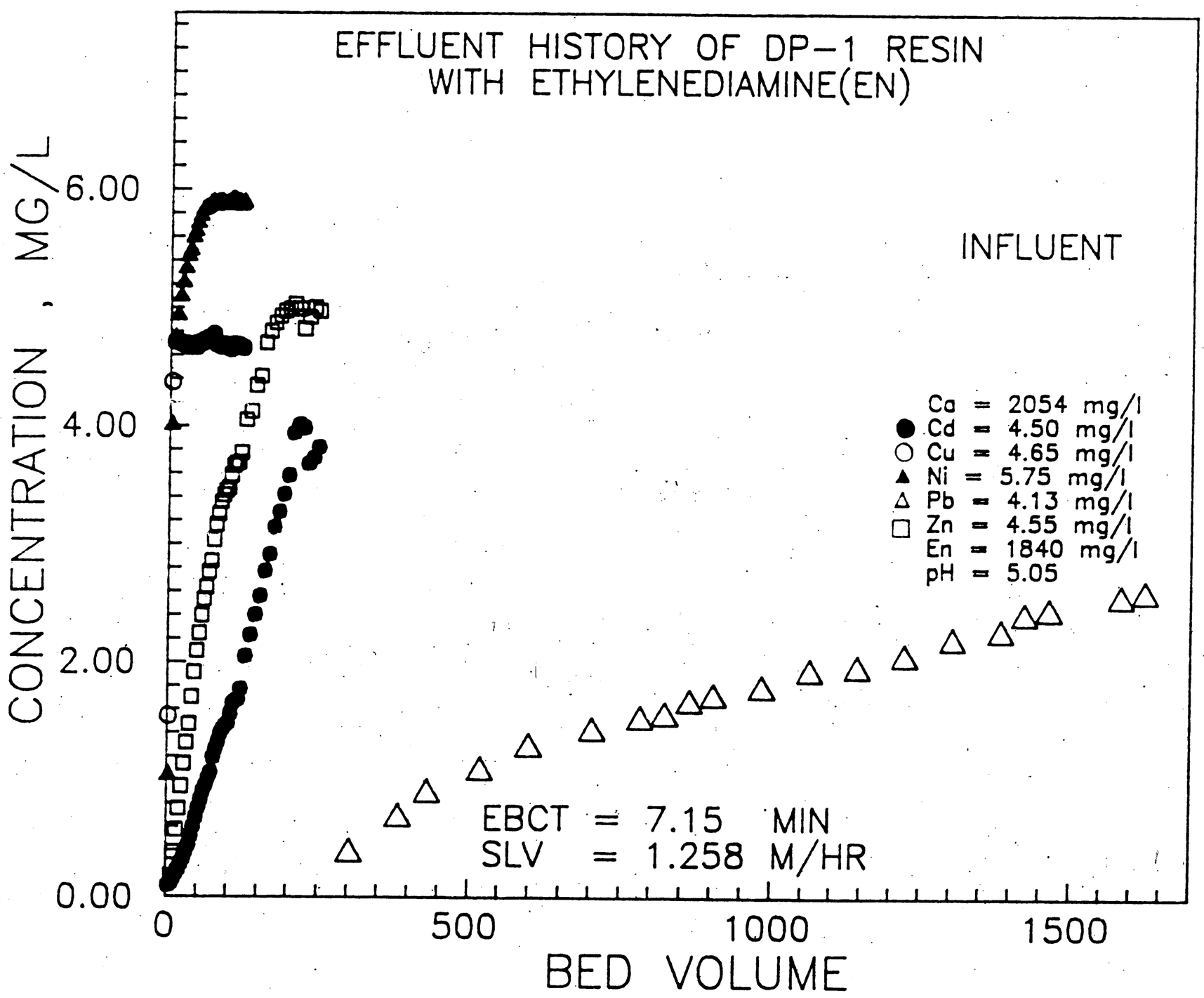


Figure 4-26: Lead Breakthrough from the Column Study with En at pH 5.0

exchange resins. Due to the chelation reaction with the ligand, the undesired metal ions would remain in the solution (aqueous phase) and would not be adsorbed on to the resin.

- Cadmium, lead and zinc are difficult to separate from one another by using En due to the narrow range of the stability constant data. Under this condition, the choice of another selective ligand for a specific metal or group of metals should be made. In contrast, due to the higher stability constant value, copper and nickel can be separated, by using En as a ligand, from the other metals studied.

- Theoretically the selectivity of ion exchange resin can be modified by (i) incorporating a stronger electronegative substituent in the neighbourhood of the functional group and (ii) by incorporating a stronger ligand. However, for a commercial resin, the second alternative is the only choice and the selectivity of the metals can be varied by adjusting the process variables, namely, making a judicious choice of the ligand itself for the application and the operating system pH.

- All the metal ions undergo complexation reaction to a great extent with En at a pH of 6.0. In order to obtain better separation among the metals by ion exchange resins, system operating pH should be kept below 6.0, preferably around 5.0. Otherwise high leakage of

the target metal ions, to be separated and recovered, from the ion exchange column would result.

- At higher pH i.e. at 5.0 the breakthrough curve of cadmium and zinc appears to be diffused instead of a comparatively sharper breakthrough curve at pH 4.0. The breakthrough curve of lead is diffused at all pH conditions of the column study.

Chapter 5
CONCLUSIONS AND RECOMMENDATION

5.1 RESEARCH CONCLUSION

From the study with the five metals and four types of chelating ion exchange resins the following conclusions can be made :

- From the application point of view, the functional group in the resin is of significant imporatance. Due to the higher selctivity for lead and copper, copolymer containing carboxylate functional group or sulfur donor atoms would be the preferred choice if lead and copper are to be separated from the other metals from a waste containing a mixture of metals. In contrast, if cadmium and zinc are to be separated from one another, resin containing nitrogen donor atoms would be the prudent choice. Due to the presence of multiple donor atoms, nitrogen and oxygen, copolymer containing iminodiacetate functional group would be the preferred choice if copper, lead and nickel were to be separated from the same waste.

- With carboxylate resin, the lead-copper separation factor decreases

from 43 at pH 4.1 to 3 at pH 6.5. The copper-zinc separation factor, in the case of resin with iminodiacetate functional group, drops from 18 to 2.5 for the same extent of change in pH. With the resin containing nitrogen donor atoms (XFS-4195), a complete reversal in selectivity is observed in the case of cadmium and nickel. The more selective nickel at pH 3.05 becomes less selective with respect to cadmium at pH 4.15. Thus, the system pH can be used as a process variable to attain the maximum separation factor in favour of the target metals to be separated and recovered. Due to improved separation factor at elevated pH, copper and lead can be effectively separated from cadmium, nickel and zinc using resin containing sulfur donor atoms. In this class of resin, pH has a little effect on the separation factor for cadmium, nickel and zinc.

- The selectivity of a commercially available ion exchange resin can be modified by incorporating a ligand in the aqueous phase. With a ligand in the aqueous phase, the more easily complexed metal remains in the solution; while the weaker complexed or uncomplexed metals can be separated by adsorbing on to the resin. The concentration of the ligand and the system pH plays an important role in the objective of modifying metal selectivity of ion exchange resins.

- At high concentration of metal ions in the aqueous phase, the amount of En required, on molar to molar basis, for the complexation of the metal in the system, is small even at a low pH. In contrast, as the metal concentration goes down in the system, the required molar ratio of En to metal for the complexation reaction goes up. Under certain operating conditions, e.g., at a metal conentration in the system in mg/l level, complete complexation is difficult to attain even adding a great amount of En at low pH. Under this circumstances, an increase in the system pH would be beneficial and would reduce the amount of En required for complexation.

- Cadmium, zinc and lead are difficult to separate from one another by using En as a ligand due to their close stability constant with En. For such applications, the proper choice of the resin functional group is of importance to attain a maximum separation factor in favour of the target metal to be separated and recovered. Alternatively, selection of a suitable ligand with a high affinity for any one or two of them, depending upon ultimate objective, would also be helpful.

5.2 SCOPE FOR FUTURE RESEARCH

Based on the present study and the observations of other investigators with metal carboxylates the followings may be identified for further study.

- From the resin titration with metal, it was observed that more than one class of binding site is responsible for binding the metal and this property appears to be dependent on the system pH and the metal involved. With carboxylate resin, more than one class of binding site is present for lead at pH 4.0. In the case of copper with carboxylate resin, at pH 5.5 more than one class of binding site was present. In contrast, resin with IDA functional group exhibits the presence of more than one class of binding site for copper at pH 4.0. A further study in this area may be made to ascertain whether covalent binding is responsible for this type of reaction or this phenomenon is due to the heterogenity in the resin composition.
- From the column study with carboxylate resin, it was observed that the breakthrough of lead is gradual not withstanding its high separation factor which should have given a sharp breakthrough. At a pH of 5.0, the breakthrough of zinc and cadmium has also become diffused (ref Fig. 5-1) in contrast to the sharp breakthrough at pH 4.0. At higher pH the selectivity of zinc and cadmium has increased. From the present study it is not clear whether the binding mechanism is playing any role at elevated pH for the diffused brekthrough characteristics of the more preferred species.

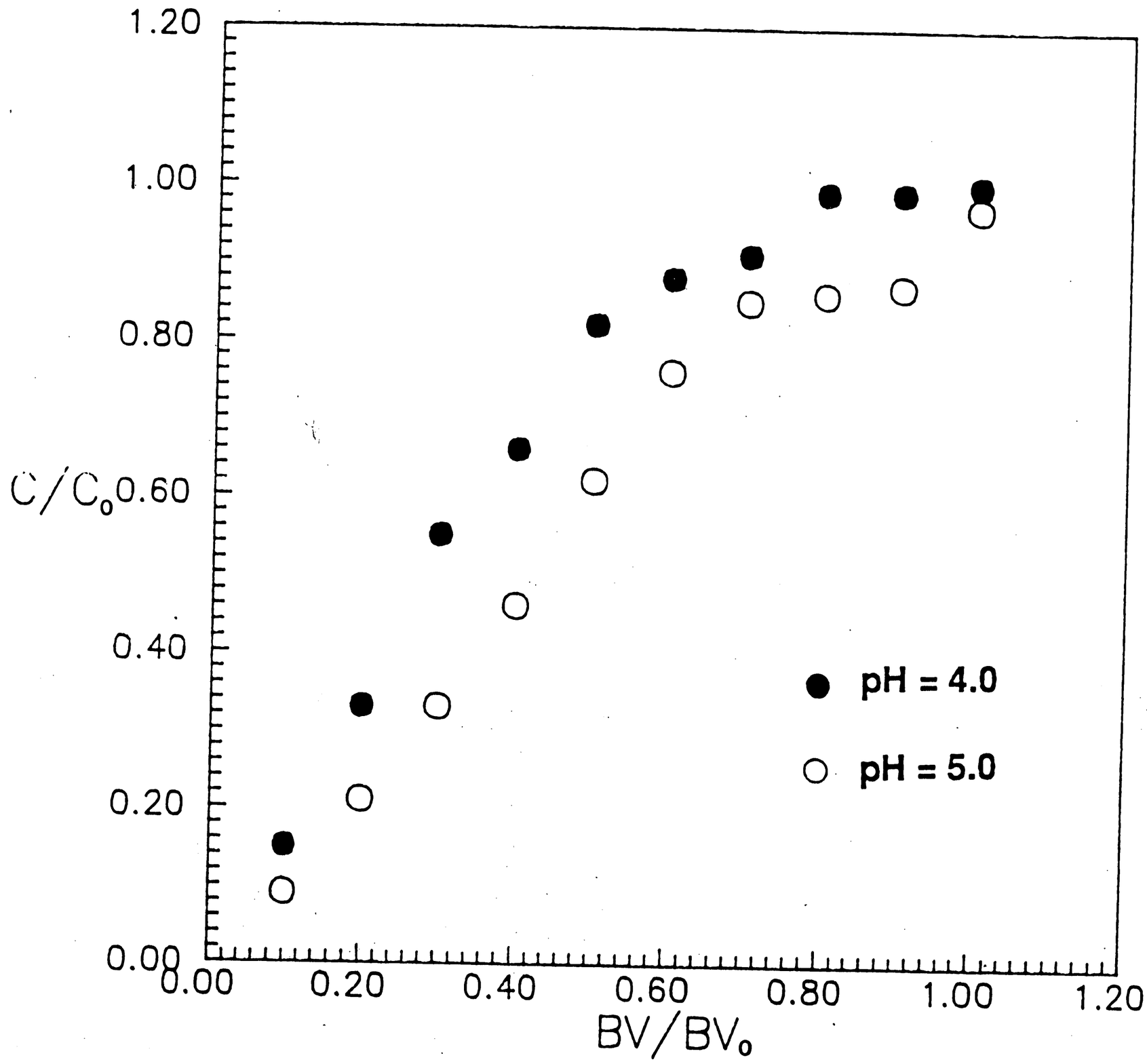


Figure 5-1: Normalised Bed Volume vs. Normalised Concentration for Cadmium at Different pH

- From the studies of other investigators it was observed that the nature of the substituent in the methyl group of carboxylates plays a key role in changing the binding mechanism of metal in addition to the nature of the apical ligand. Based on this, new breed of chelating ion exchange resins can be developed containing suitable substituent for further study towards improved separation and recovery of metals.

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Appendix A
EQUILIBRIUM STUDY OF METAL IONS WITH CARBOXYLATE RESIN AT A pH OF 4.1

WT. OF RESIN TAKEN (GM.) = .5250

RESIN REGENERATION VOL. (LIT.) = .20

COUNTER ION	AQUEOUS PHASE CONCENTRATION (MG/L)	AQUEOUS PHASE CONCENTRATION (MEQ./L)	RES.PHASE CONC. (MG/L)	RES.PHASE MASS (MEQ)	AQ.PHASE FRACN.	RES.PHASE FRACN.	SELECTIVITY	SEPARATION FACTOR ALPHA(ME2+/CA
CA2+	.553E+03	.276E+02	.175E+02	.175E+00	.100E+01	.957E+00	.96	1.00
CD2+	.105E+00	.187E-02	.168E-01	.598E-04	.676E-04	.328E-03	4.85	5.06
CU2+	.936E-01	.295E-02	.122E+00	.766E-03	.107E-03	.421E-02	39.50	41.24
NI2+	.107E+00	.364E-02	.750E-02	.511E-04	.132E-03	.280E-03	2.13	2.22
PB2+	.610E-01	.588E-03	.345E+01	.666E-02	.213E-04	.365E-01	1714.33	1789.88
ZN2+	.976E-01	.299E-02	.400E-01	.245E-03	.108E-03	.134E-02	12.42	12.97

CAPACITY OF DP-1 RESIN AT PH 4.10 (IN MEQ/GM) = .347

Appendix B
EQUILIBRIUM STUDY OF METAL IONS WITH CARBOXYLATE RESIN AT A pH OF 6.52

WT. OF RESIN TAKEN (GM.) = .2033

RESIN REGENERATION VOL, (LIT.) = .20

COUNTER ION	AQUEOUS PHASE CONCENTRATION (MG/L)	AQUEOUS PHASE CONCENTRATION (MEQ./L)	RES.PHASE CONC. (MG/L)	RES.PHASE MASS (MEQ)	AQ.PHASE FRACN.	RES.PHASE FRACN.	SELECTIVITY	SEPARATION FACTOR ALPHA(ME2+/CA
CA2+	.553E+03	.276E+02	.102E+03	.102E+01	.100E+01	.865E+00	.87	1.00
CD2+	.105E+00	.187E-02	.367E+01	.131E-01	.676E-04	.111E-01	164.05	189.60
CO2+	.936E-01	.295E-02	.148E+02	.934E-01	.107E-03	.793E-01	744.03	859.93
NI2+	.107E+00	.364E-02	.481E-01	.328E-03	.132E-03	.278E-03	2.11	2.44
PB2+	.610E-01	.588E-03	.250E+02	.483E-01	.213E-04	.410E-01	1928.46	2228.88
ZN2+	.976E-01	.299E-02	.678E+00	.415E-02	.108E-03	.352E-02	32.62	37.70

CAPACITY OF DP-1 RESIN AT PH 6.52 (IN MEQ/GM) = 5.794

Appendix C
EQUILIBRIUM STUDY OF METAL IONS WITH XFS-4195 RESIN AT pH 3.05

EQUILIBRIUM SYSTEM PH = 3.05

WT. OF RESIN TAKEN (GM.) = .5012

RESIN REGENERATION VOL, (LIT.) = .50

COUNTER ION	AQUEOUS PHASE CONCENTRATION (MG/L)	(MEQ./L)	RES.PHASE CONC. (MG/L)	RES.PHASE MASS (MEQ)	AQ. PHASE FRACN.	RES.PHASE FRACN.	SELECTIVITY	SEPARATION FACTOR ALPHA(ME2+/CA
CA2+	.448E+03	.224E+02	.200E+00	.500E-02	.994E+00	.108E-01	.01	1.00
CO2+	.945E+00	.168E-01	.281E+01	.251E-01	.747E-03	.541E-01	72.50	6660.74
CU2+	.883E+00	.278E-01	.201E+02	.316E+00	.123E-02	.685E+00	554.97	50989.81
NI2+	.114E+01	.406E-01	.642E+01	.109E+00	.180E-02	.237E+00	131.20	12054.32
PB2+	.107E+01	.103E-01	.250E+00	.121E-02	.456E-03	.261E-02	5.72	525.82
ZN2+	.943E+00	.289E-01	.330E+00	.505E-02	.128E-02	.109E-01	8.53	783.88

CAPACITY OF XFS-4195 (NU3- FORM) RESIN AT PH 3.05 (IN MEQ/GM) = .922

Appendix D
EQUILIBRIUM STUDY OF METAL IONS WITH RESIN XFS-4195 AT pH 4.15

EQUILIBRIUM SYSTEM PH = 4.15

WT. OF RESIN TAKEN (GM.) = .5004

RESIN REGENERATION VOL, (LIT.) = .50

COUNTER ION	AQUEOUS PHASE CONCENTRATION (MG/L)	(MEQ./L)	RES.PHASE CONC. (MG/L)	RES.PHASE MASS (MEQ)	AQ.PHASE FRACN.	RES.PHASE FRACN.	SELECTIVITY	SEPARATION FACTOR ALPHA(ME2+/CA
CA2+	.448E+03	.224E+02	.410E+00	.103E-01	.994E+00	.243E-01	.02	1.00
CD2+	.945E+00	.168E-01	.430E+01	.383E-01	.747E-03	.905E-01	121.26	4972.00
CU2+	.883E+00	.278E-01	.185E+02	.290E+00	.123E-02	.687E+00	556.83	22831.26
NI2+	.119E+01	.406E-01	.385E+01	.656E-01	.180E-02	.155E+00	86.00	3526.26
PB2+	.107E+01	.103E-01	.370E+00	.179E-02	.456E-03	.423E-02	9.26	379.62
ZN2+	.943E+00	.289E-01	.107E+01	.164E-01	.128E-02	.387E-01	30.24	1239.84

CAPACITY OF XFS-4195 (NO3- FORM) RESIN AT PH 4.15 (IN MEQ/GM) = .845

Appendix E

EQUILIBRIUM STUDY OF METAL IONS WITH RESIN XFS-4195 AT pH 5.15

EQUILIBRIUM SYSTEM PH = 5.15

WT. OF RESIN TAKEN (GM.) = .4996

RESIN REGENERATION VOL, (LIT.) = .50

COUNTER ION	AQUEOUS PHASE CONCENTRATION (MG/L)	(MEQ./L)	RES.PHASE CONC. (MG/L)	RES.PHASE MASS (MEQ)	AQ.PHASE FRACN.	RES.PHASE FRACN.	SELECTIVITY	SEPARATION FACTOR ALPHA(ME2+/CA
CA2+	.448E+03	.224E+02	.380E+00	.950E-02	.994E+00	.274E-01	.03	1.00
CO2+	.945E+00	.168E-01	.373E+01	.332E-01	.747E-03	.959E-01	128.44	4653.41
CU2+	.883E+00	.278E-01	.150E+02	.235E+00	.123E-02	.680E+00	550.95	19960.66
NI2+	.119E+01	.406E-01	.278E+01	.474E-01	.180E-02	.137E+00	75.83	2747.25
PB2+	.107E+01	.103E-01	.532E+00	.257E-02	.456E-03	.742E-02	16.26	588.92
ZN2+	.943E+00	.289E-01	.119E+01	.182E-01	.128E-02	.526E-01	41.06	1487.75

CAPACITY OF XFS-4195 (NO3- FORM) RESIN AT PH 5.15 (IN MEQ/GM) = .693

Appendix F

EQUILIBRIUM STUDY OF METAL IONS WITH RESIN GT-73 AT pH 4.1

EQUILIBRIUM SYSTEM PH = 4.10

WT. OF RESIN TAKEN (GM.) = .5010

RESIN REGENERATION VOL. (LIT.) = .20

COUNTER ION	AQUEOUS PHASE CONCENTRATION (MG/L)	(MEQ./L)	RES.PHASE CONC. (MG/L)	RES.PHASE MASS (MEQ)	AQ.PHASE FRACN.	RES.PHASE FRACN.	SELECTIVITY	SEPARATION FACTOR ALPHA(ME2+/CA)
CA2+	.553E+03	.276E+02	.747E+02	.747E+00	.100E+01	.968E+00	.97	1.00
CD2+	.105E+00	.187E-02	.482E-01	.172E-03	.676E-04	.222E-03	3.29	3.40
CU2+	.936E-01	.295E-02	.269E+01	.169E-01	.107E-03	.219E-01	206.00	212.66
NI2+	.107E+00	.364E-02	.215E-01	.147E-03	.132E-03	.190E-03	1.45	1.49
PB2+	.610E-01	.588E-03	.358E+01	.691E-02	.213E-04	.896E-02	421.40	435.04
ZN2+	.976E-01	.299E-02	.550E-01	.337E-03	.108E-03	.437E-03	4.04	4.17

CAPACITY OF GT-73 RESIN AT PH 4.10 (IN MEQ/GM) = 1.539

Appendix G

EQUILIBRIUM STUDY OF METAL IONS WITH RESIN GT-73 AT pH 5.15

EQUILIBRIUM SYSTEM PH = 5.15

WT. OF RESIN TAKEN (GM.) = .5000

RESIN REGENERATION VOL. (LIT.) = .20

COUNTER ION	AQUEOUS PHASE CONCENTRATION (MG/L)	(MEQ./L)	RES.PHASE CONC. (MG/L)	RES.PHASE MASS (MEQ)	AQ.PHASE FRACN.	RES.PHASE FRACN.	SELECTIVITY	SEPARATION FACTOR ALPHA(ME2+/CA
CA2+	.553E+03	.276E+02	.798E+02	.798E+00	.100E+01	.922E+00	.92	1.00
CD2+	.105E+00	.187E-02	.130E+00	.463E-03	.676E-04	.535E-03	7.92	8.58
CU2+	.936E-01	.295E-02	.721E+01	.454E-01	.107E-03	.525E-01	492.50	533.83
NI2+	.107E+00	.364E-02	.883E+00	.602E-02	.132E-03	.695E-02	52.86	57.30
PB2+	.610E-01	.588E-03	.765E+01	.148E-01	.213E-04	.171E-01	802.48	869.83
ZN2+	.976E-01	.299E-02	.115E+00	.704E-03	.108E-03	.813E-03	7.53	8.17

CAPACITY OF GT-73 RESIN AT PH 5.15 (IN MEQ/GM) = 1.730

Appendix H
EQUILIBRIUM STUDY OF METAL IONS WITH RESIN GT-73 AT pH 6.52

EQUILIBRIUM SYSTEM PH = 6.52

WT. OF RESIN TAKEN (GM.) = .2053

RESIN REGENERATION VOL, (LIT.) = .20

COUNTER ION	AQUEOUS PHASE CONCENTRATION (MG/L)	(MEQ./L)	RES.PHASE CONC. (MG/L)	RES.PHASE MASS (MEQ)	AQ.PHASE FRACN.	RES.PHASE FRACN.	SELECTIVITY	SEPARATION FACTOR ALPHA(ME2+/CA)
CA2+	.553E+03	.276E+02	.309E+02	.309E+00	.100E+01	.906E+00	.91	1.00
CD2+	.105E+00	.187E-02	.246E-01	.875E-04	.676E-04	.257E-03	3.80	4.19
CU2+	.936E-01	.295E-02	.372E+01	.234E-01	.107E-03	.687E-01	644.70	711.14
NI2+	.107E+00	.364E-02	.492E-01	.335E-03	.132E-03	.982E-03	7.47	8.24
PB2+	.610E-01	.588E-03	.405E+01	.783E-02	.213E-04	.229E-01	1078.08	1189.18
ZN2+	.976E-01	.299E-02	.540E-01	.330E-03	.108E-03	.968E-03	8.97	9.89

CAPACITY OF GT-73 RESIN AT PH 6.52 (IN MEQ/GM) = 1.662

Appendix I
EQUILIBRIUM STUDY OF METAL IONS WITH IMINODIACETATE RESIN AT A pH OF 4.1

WT. OF RESIN TAKEN (GM.) = .5193

RESIN REGENERATION VOL. (LIT.) = .20

COUNTER ION	AQUEOUS PHASE CONCENTRATION (MG/L)	AQUEOUS PHASE CONCENTRATION (MEQ./L)	RES.PHASE CONC. (MG/L)	RES.PHASE MASS (MEQ)	AQ.PHASE FRACN.	RES.PHASE FRACN.	SELECTIVITY	SEPARATION FACTOR ALPHA(ME2+/CA)
CA2+	.553E+03	.276E+02	.100E+03	.100E+01	.100E+01	.616E+00	.62	1.00
CO2+	.103E+00	.187E-02	.175E+01	.622E-02	.676E-04	.383E-02	56.63	91.83
CU2+	.936E-01	.295E-02	.609E+02	.383E+00	.107E-03	.236E+00	2213.22	3589.06
NI2+	.107E+00	.364E-02	.233E+02	.159E+00	.132E-03	.978E-01	743.58	1205.8
PB2+	.610E-01	.588E-03	.275E+02	.531E-01	.213E-04	.327E-01	1536.87	2492.2
ZN2+	.976E-01	.299E-02	.359E+01	.219E-01	.108E-03	.135E-01	125.12	202.9

CAPACITY OF IRC-718 RESIN AT PH 4.10 (IN MEQ/GM) = 3.129

Appendix J
EQUILIBRIUM STUDY OF METAL IONS WITH IMINODIACETATE RESIN AT A pH OF 5.15

EQUILIBRIUM SYSTEM PH = 5.15

WT. OF RESIN TAKEN (GM.) = .4984

RESIN REGENERATION VOL. (LIT.) = .20

COUNTER ION	AQUEOUS PHASE CONCENTRATION (MG/L)	AQUEOUS PHASE CONCENTRATION (MEQ./L)	RES.PHASE CONC. (MG/L)	RES.PHASE MASS (MEQ)	AQ.PHASE FRACN.	RES.PHASE FRACN.	SELECTIVITY	SEPARATION FACTOR ALPHA(ME2+/CA)
CA2+	.553E+03	.276E+02	.798E+02	.798E+00	.100E+01	.470E+00	.47	1.00
CO2+	.105E+00	.187E-02	.785E+01	.279E-01	.676E-04	.165E-01	243.61	518.03
CU2+	.936E-01	.295E-02	.768E+02	.483E+00	.107E-03	.285E+00	2671.19	5680.24
NI2+	.107E+00	.364E-02	.350E+02	.238E+00	.132E-03	.140E+00	1065.91	2266.65
PB2+	.610E-01	.588E-03	.386E+02	.744E-01	.213E-04	.438E-01	2060.68	4381.99
ZN2+	.976E-01	.299E-02	.125E+02	.702E-01	.108E-03	.449E-01	415.70	883.97

CAPACITY OF IRC-718 RESIN AT PH 5.15 (IN MEQ/GM) = 3.407

Appendix K
EQUILIBRIUM STUDY OF METAL IONS WITH IMINODIACETATE RESIN AT A pH OF 6.52

EQUILIBRIUM SYSTEM PH = 6.52

WT. OF RESIN TAKEN (GM.) = .2011

RESIN REGENERATION VOL, (LIT.) = .20

COUNTER ION	AQUEOUS PHASE CONCENTRATION (MG/L)	AQUEOUS PHASE CONCENTRATION (MEQ./L)	RES.PHASE CONC. (MG/L)	RES.PHASE MASS (MEQ)	AQ.PHASE FRACN.	RES.PHASE FRACN.	SELECTIVITY	SEPARATION FACTOR ALPHA(ME2+/CA)
CA2+	.553E+03	.276E+02	.469E+02	.409E+00	.100E+01	.531E+00	.53	1.00
CO2+	.105E+00	.187E-02	.338E+01	.298E-01	.676E-04	.338E-01	500.27	941.07
CU2+	.936E-01	.295E-02	.268E+02	.168E+00	.107E-03	.191E+00	1790.97	3369.02
NI2+	.107E+00	.364E-02	.163E+02	.111E+00	.132E-03	.126E+00	957.87	1801.85
PB2+	.610E-01	.588E-03	.183E+02	.353E-01	.213E-04	.400E-01	1878.26	3533.22
ZN2+	.976E-01	.299E-02	.213E+02	.689E-01	.108E-03	.781E-01	723.27	1360.56

CAPACITY OF IRC-718 RESIN AT PH 6.52 (IN MEQ/GM) = 4.390

Appendix L
DISTRIBUTION OF METAL SPECIES IN WATER

L.1 METAL ION SOLUBILITY

The solubility of a metal in water is dependent on pH. The metals remain in solution upto a certain pH of the system. Exceeding that limiting pH condition, the metals precipitate out from the system as metal hydroxides. Besides, the hydroxyl ions present in water, form monovalent and higher valence complexes with the metals. In this section the disrtribution of metals species in aqueous phase at different pH conditions of the aqueous media is established. To calculate the different metal species concentration it is considered that the water is pure water without any dissolved constituents. It is also considered that the system is an ideal one and hence the ionic strength effects have been ignored.

L.1.1 Solubility Product

The solubility product is an equilibrium relationship between the cationic and anionic part of a molecule in the dissolved state in aqueous phase. For dissolved metals in water, the solubility products relationship dictate the maximum concentration of the free metals that can be present at a particular pH. Ideally product of activities of the cationic and anionic part of a molecule is the solubility product. Since ideal system has been considered, activities are

replaced by the concentration of the metals and hydroxyl ions. Mathematically one can then define the solubility products of metal ions in water as:

$$M^{2+} . (OH^{-2}) = K_{SP} \quad \text{(L.1)}$$

Where,

M^{2+} = Metal ion present in water

OH^- = Hydroxyl ion concentration

K_{SP} = Solubility Product

In the above equation both the metal ion concentration and hydroxyl ion concentration are expressed as mole per litre. Thus from the knowledge of system pH and solubility product, the maximum permissible metal ion concentration in pure aqueous media can be determined from Eq. (L.1)

L.1.2 Metal-Hydroxyl Complexes

Hydroxyl ions also form coordination complexes with metal ions. Due to these complex formation reactions between metal ions and hydroxyl ions, a number of different charged and neutral species are formed in the aueous phase. These complex formation reactions also affect the solubilities of the metal ions. The complex formation reactions between metal ions and hydroxyl ions can be represented as follows:

$$M^{2+} + (OH^-) = M(OH)^+, \quad K_{ST1} \quad \text{(L.2)}$$

$$M(OH)^+ + (OH^-) = M(OH)_2, \quad K_{ST2} \quad \text{(L.3)}$$

$$M(OH)_2 + (OH^-) = M(OH)^-_3, \quad K_{ST3} \quad \text{(L.4)}$$

$$M(OH)_3^- + (OH^-) = M(OH)_4^{2-},\ K_{ST4} \qquad \text{(L.5)}$$

Where, K_{ST1} to K_{ST4} are the step wise stability constants for the reactions given in Eqn. (L.2) to Eqn. (L.5) above.

The reactions given by Eqn. (L.4) and Eqn. (L.5) are predominant when the aqueous phase pH are at and above 10.0. In the metal solubility calculations it is considered only the first two complexation reactions i.e. reactions given by Eqn. (L.2) and Eqn. (L.3) because in the experimental studies the pH encountered was at 7.0.

L.2 SPECIES DISTRIBUTION

Equations (L.1) to (L.3) above describes the equilibrium relationshaip among the metal ions, hydroxyl ions and the metal-hydroxide complex ions in aqueous phase. Simultaneous solving of these three equations will limit the maximum permissible concentration of any species at a given pH of the aqueous phase.

L.2.1 Distribution of Cadmium Species

For the speciation calculation for the cadmium ion, the values of K_{SP} [13], K_{ST1} and K_{ST2} [44] have been considered as 5.27E-15 , 7.94E3 and 3.98E7 respectively. The concentrations of various species are presented in Figure L-1 as a function of pH. The maximum metal ion concentration at pH 6 and 7 are given in Table L-1. The cadmium ion concentration at pH 7.0 is about 51.3 gm/l.

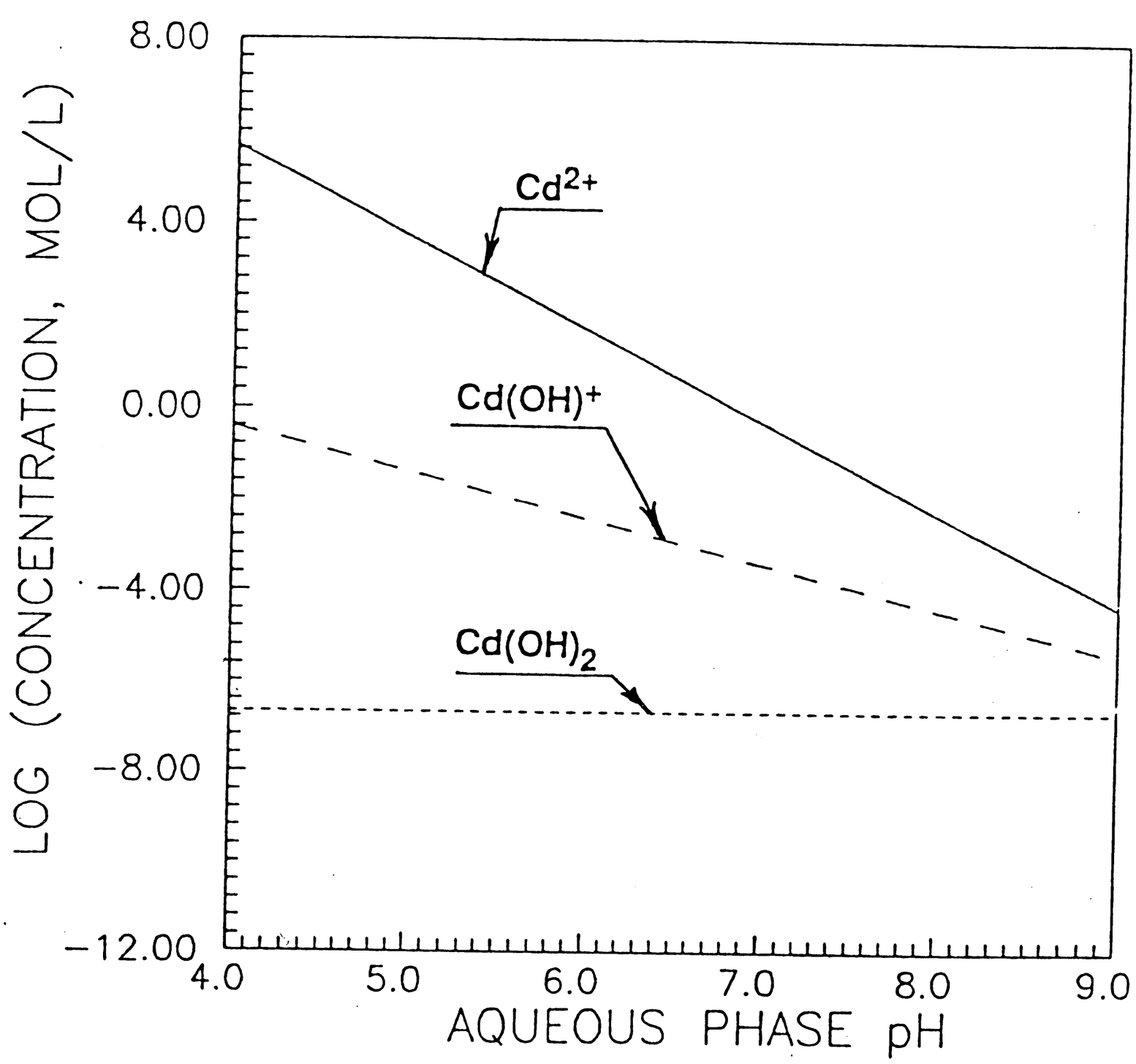

Figure L-1: pH vs. the Distribution of Cadmium Species in Aqueous Phase

L.2.2 Distribution of Copper Species

The speciation of various copper complexes in aqueous media are calculated based on the K_{SP} [41], K_{ST1} and K_{ST2} [44] values of 2.E-19 , 3.16E6 and 6.31E11 respectively. The concentrations of various copper species in aqueous phase are presented in Figure L-2. The maximum concentration of copper ion is 1.27 mg/l at a pH of 7.0.

L.2.3 Distribution of Nickel Species

The solubility product [41], the first and the second stability constant [44] for nickel have been considered as 2.E-16, 1.26E4 and 1.E9 respectively. Concentrations of nickel species in aqueous media are presented in Figure L-3. At pH 7.0, maximum nickel ion concentration in pure water is 1.17 gm/l.

L.2.4 Speciation of Lead in Water

The solubility product [13] and the two stability constants [44] data of lead have been considered as 1.42E-20, 1.99E6 and 7.94E10 respectively. The concentrations of the aqueous lead species are given in Figure L-4. 0.294 mg/l is the maximum concentration of the lead ion in water at pH 7.0.

L.2.5 Distribution of Zinc Species

The K_{SP} [41], K_{ST1} and K_{ST2} [44] constants for zinc have been taken as 3.E-17, 1.E5 and 1.26E11 respectively to calculate the various zinc species concentration in aqueous media. The concentration of the aqueous zinc species are plotted in Figure L-5. Zinc ion has a maximum concentration of 0.196 gm/l re in pure water at a pH of 7.0.

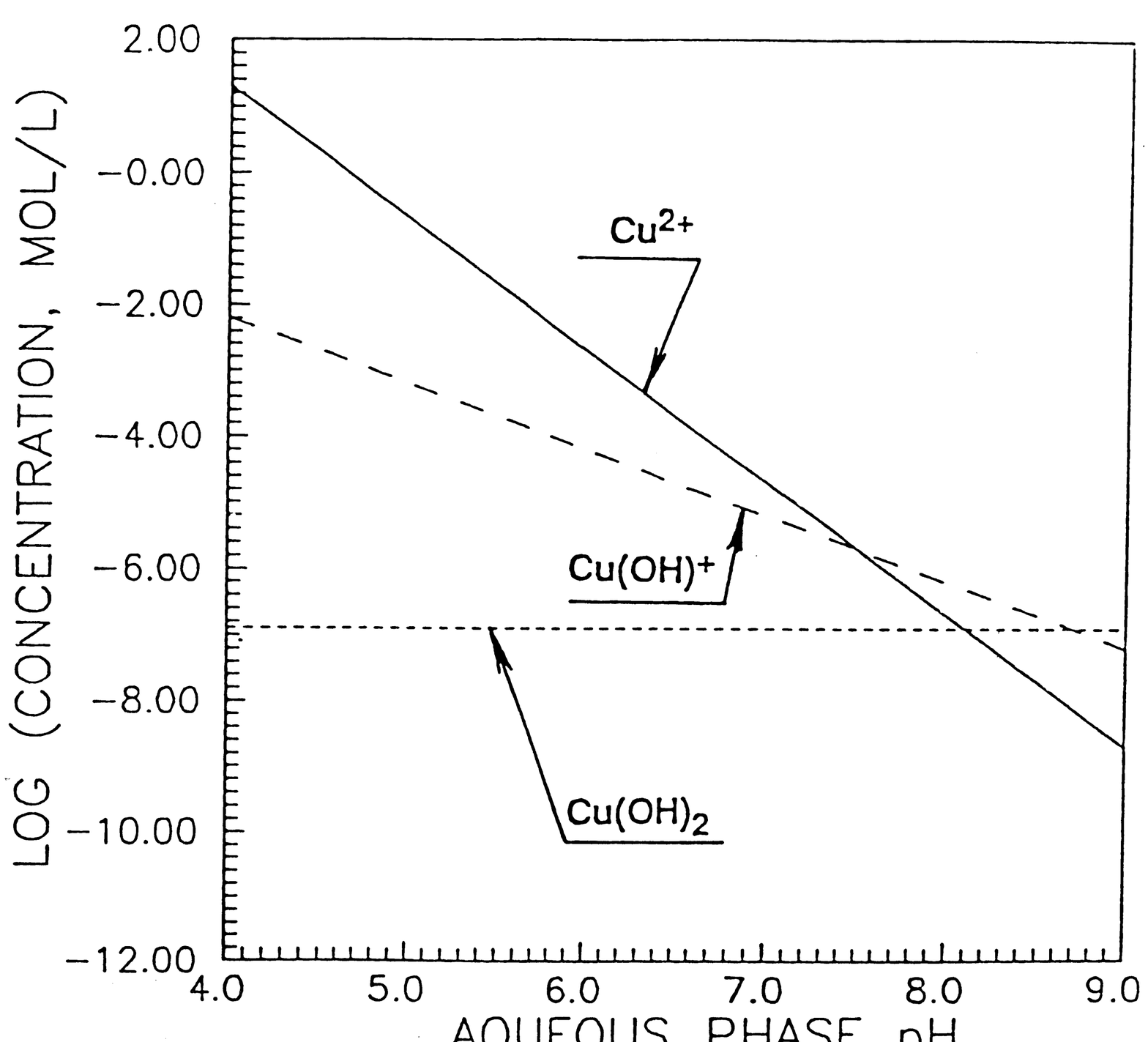

Figure L-2: pH vs. the Distribution of Copper Species in Aqueous Phase

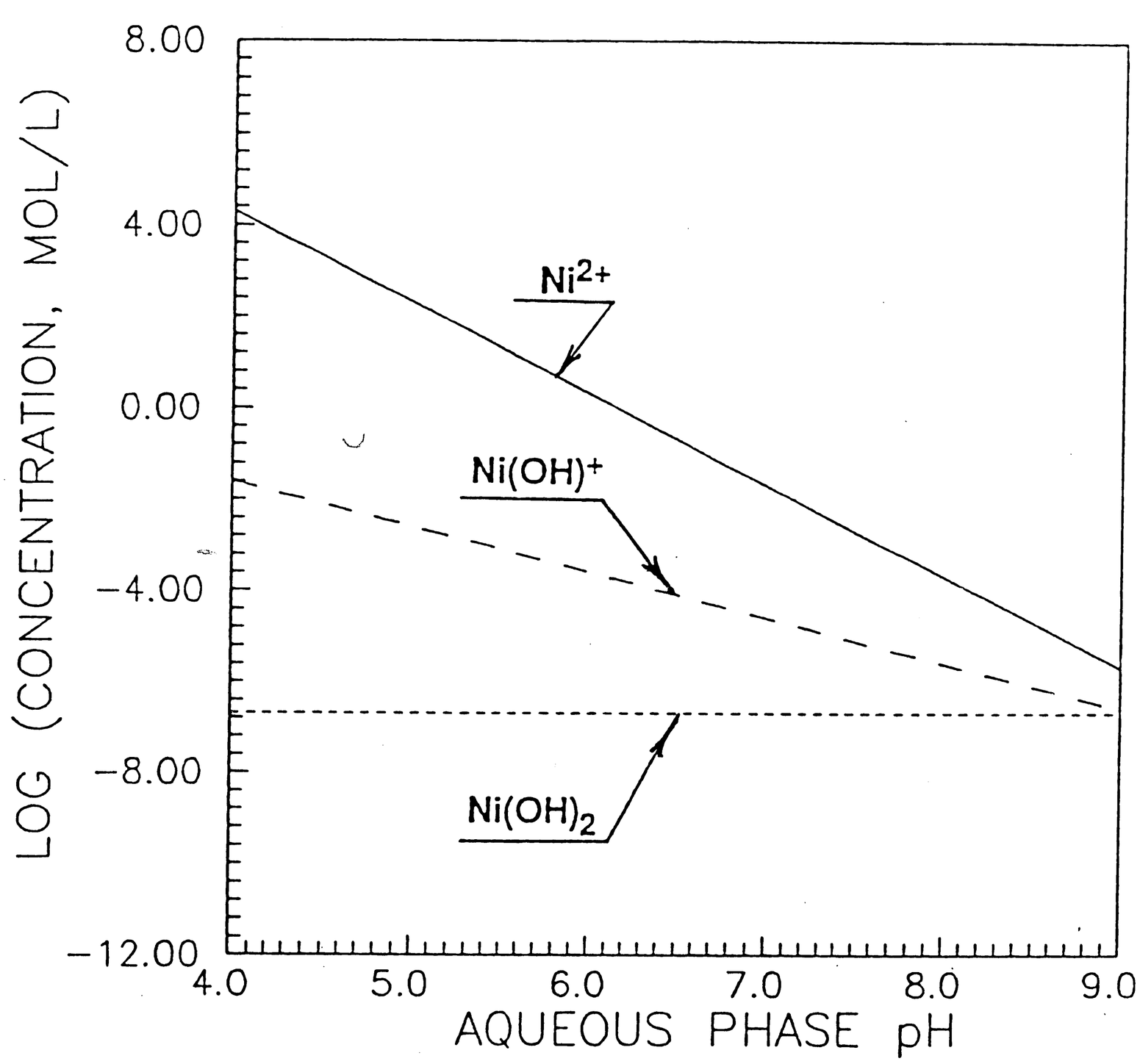

Figure L-3: pH vs. the Distribution of Nickel Species in Aqueous Phase

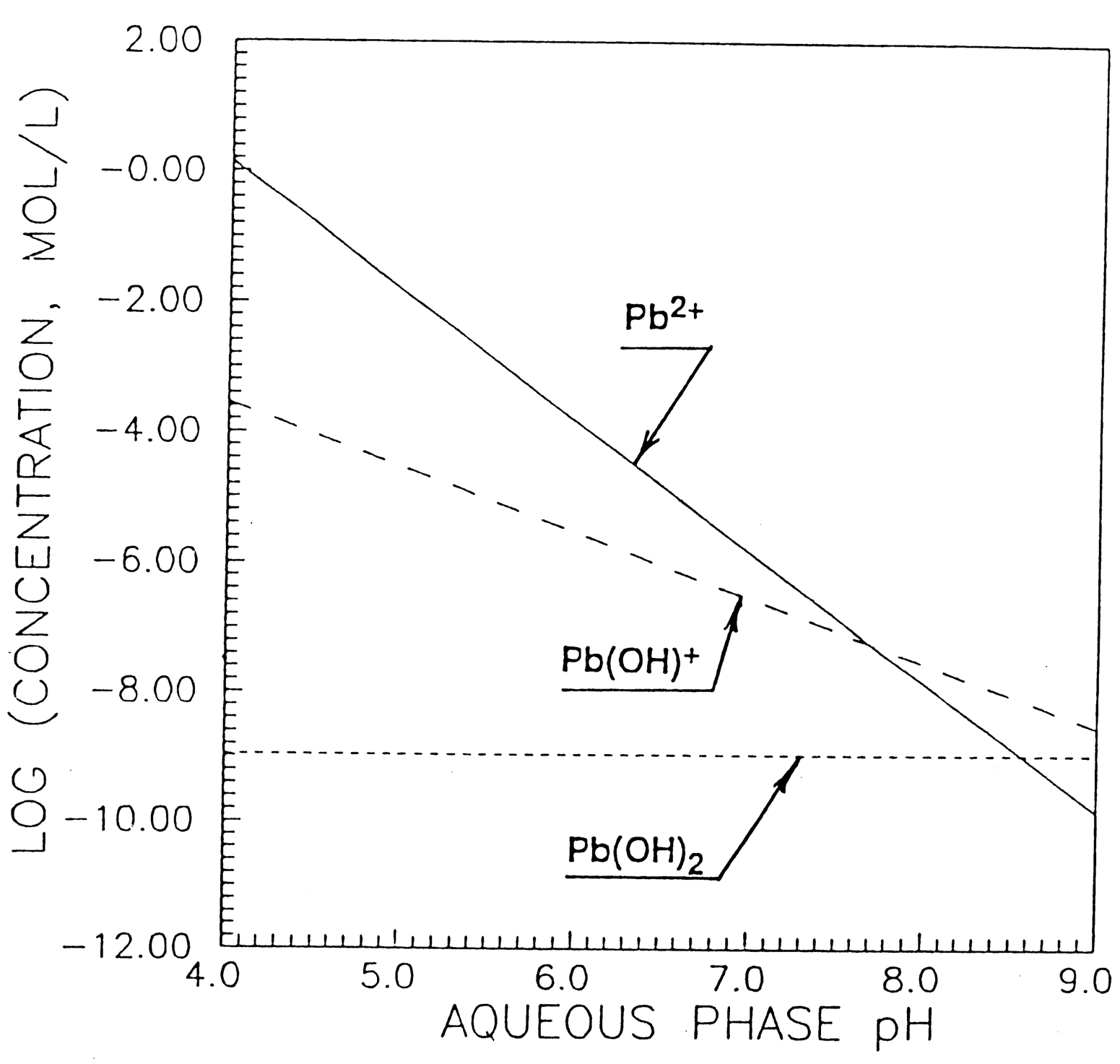

Figure L-4: pH vs. the Distribution of Lead Species in Aqueous Phase

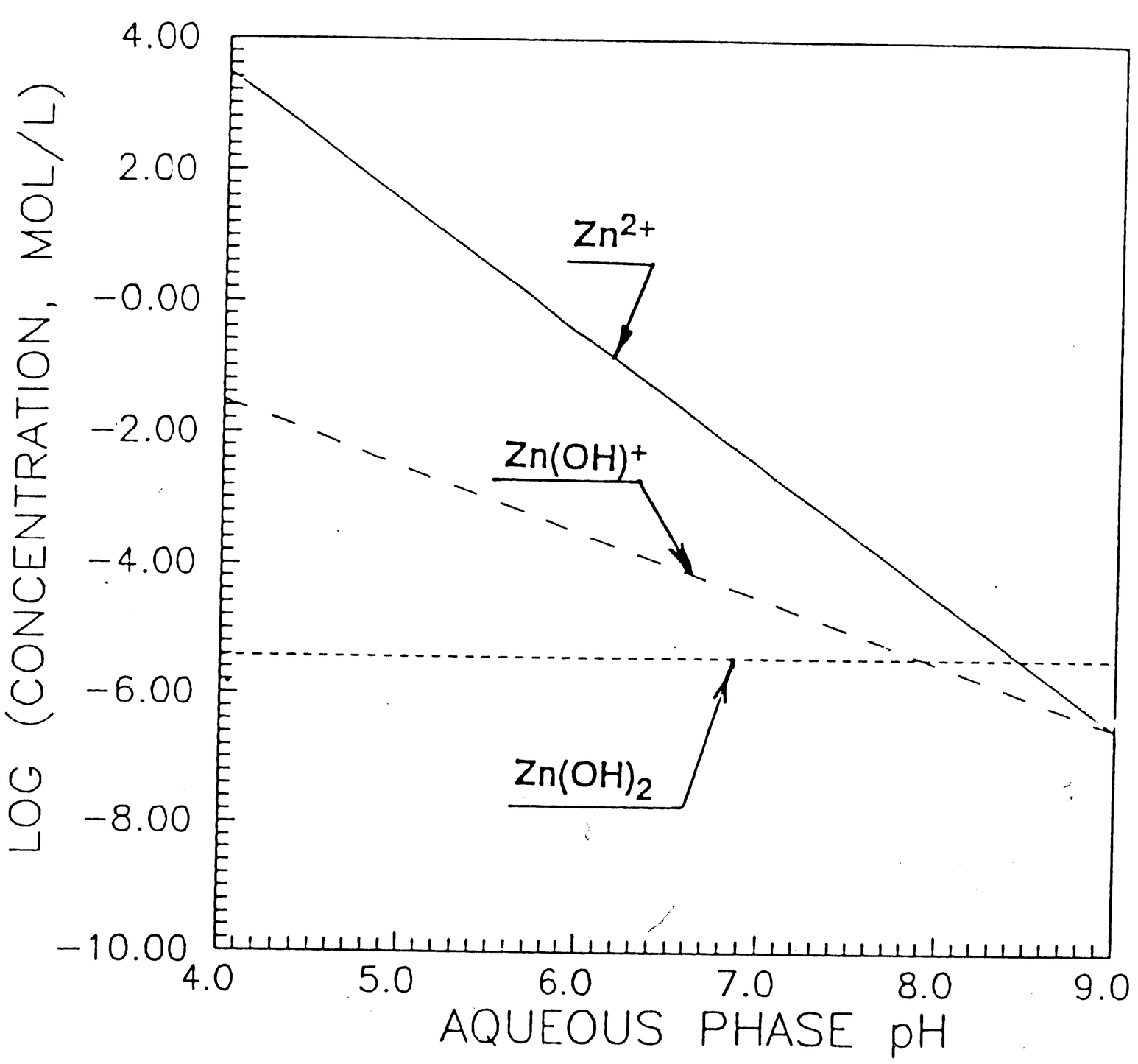

Figure L-5: pH vs. the Distribution of Zinc Species in Aqueous Media

Table L-1: pH vs. the Maximum Free Metal Ion Solubility in the Aqueous Phase

Metal Ion	Solubility at pH=6.0	Solubility at pH=7.0
Cadmium (Cd^{2+})	5.13E6 mg/litre	5.13E4 mg/litre
Copper (Cu^{2+})	1.27E2 mg/litre	1.27 mg/litre
Nickel (Ni^{2+})	1.17E5 mg/litre	1.17E3 mg/litre
Lead (Pb^{2+})	2.94E1 mg/litre	0.294 mg/litre
Zinc (Zn^{2+})	1.96E4 mg/litre	1.96E2 mg/litre

L.3 OBSERVATIONS

From Figure L-1 to Figure L-5 and also from Table L-1 it is observed that lead ion has the minimum solubility and cadmium ion has the maximum solubility among the five metals considered. In the order of decreasing concentration at a given pH, the metal ions can be ranked as follows:

Cadmium (Cd^{2+}) > Nickel (Ni^{2+}) > Zinc (Zn^{2+}) > Copper (Cu^{2+}) > Lead (Pb^{2+})

The limiting solubility of the metal ions increases by two order of magnitudes by lowering the pH by one unit. Similarly the metal ion solubility decreases by two order of magnitude for one unit increase in aqueous phase pH.

Appendix M
TITTRATION OF BIO-REX 70 WITH COPPER AT pH 4.0 WITH 0.048M SODIUM NITRATE

WT. OF RESIN TAKEN = 3.68200

ORIGINAL TITRATION SYSTEM VOL.,ML. = 500.00000

CONCENTRATION OF TITRANT = 794.000 AS CU IN MG/LIT

BACKGROUND NANO3 CONC. = 0.048 M

SL. NO.	NAOH ADDED (ML)	SAM. VOL. (ML)	TITRANT ADDED (ML)	TITRANT ADDED (MMOL,TOT.)	AQ. PHASE CONC. (MG/L)	AQ. PHASE CONC. (MMOL/L(M))	RESIN UPTAKE (MMOL)	RESIN UPTAKE (MMOL/GM(MR))	MR/M	V	V/M
1	3.10	10.0	10.0	.125E+00	.758E+01	.119E+00	.638E-01	.173E-01	.145E+00	$5X10^{-3}$	41.85
2	2.90	10.0	10.0	.250E+00	.135E+02	.244E+00	.127E+00	.346E-01	.142E+00	$9.9X10^{-3}$	40.7

3	2.70	10.0	.3756E+00	.2376E+02	.3736E+00	.1876E+00	.5096E-01	.1366+00	1.5×10^{-2}	39.1
4	2.30	10.0	.5006+00	.3296+02	.5186+00	.2406+00	.6516-01	.1266+00	1.9×10^{-2}	36.3
5	2.10	20.0	.6256+00	.4236+02	.6666+00	.2916+00	.7896-01	.1196+00	2.3×10^{-2}	34.1
6	2.00	10.0	.7506+00	.5186+02	.8156+00	.3496+00	.9476-01	.1166+00	2.7×10^{-2}	33.5
7	2.00	10.0	.8756+00	.6156+02	.9686+00	.3896+00	.1066+00	.1096+00	3×10^{-2}	31.4
8	1.50	10.0	.1006+01	.7186+02	.1136+01	.4536+00	.1186+00	.1046+00	3.4×10^{-2}	30.
9	1.40	10.0	.1126+01	.8296+02	.1306+01	.4746+00	.1296+00	.9916-01	3.7×10^{-2}	28.5
10	1.20	20.0	.1256+01	.9206+02	.1456+01	.5246+00	.1426+00	.9836-01	4.1×10^{-2}	28.2
11	2.40	20.0	.1506+01	.1136+03	.1786+01	.6386+00	.1656+00	.9306-01	4.7×10^{-2}	26.7
12	1.90	20.0	.1756+01	.1346+03	.2116+01	.6936+00	.1886+00	.8936-01	5.4×10^{-2}	25.6
13	1.90	20.0	.2006+01	.1556+03	.2456+01	.7726+00	.2106+00	.8576-01	6×10^{-2}	24.6
14	1.60	20.0	.2256+01	.1756+03	.2766+01	.8056+00	.2356+00	.8516-01	6.8×10^{-2}	24.5
15	1.60	20.0	.2506+01	.1956+03	.3086+01	.9576+00	.2606+00	.8456-01	7.5×10^{-2}	24.3
16	1.60	20.0	.2756+01	.2146+03	.3376+01	.1066+01	.2876+00	.8506-01	8.3×10^{-2}	24.5
17	1.70	20.0	.3006+01	.2346+03	.3716+01	.1146+01	.3096+00	.8346-01	8.9×10^{-2}	24.0

Appendix N

TITRATION OF BIO-REX 70 WITH COPPER AT pH 4.0 WITH 0.11M SODIUM NITRATE

WT. OF RESIN TAKEN = 5.3146O

ORIGINAL TITRATION SYSTEM VOL.,ML. = 500.00000

CONCENTRATION OF TITRANT = 121.000 AS CU IN MG/LI?

BACKGROUND NANO3 CONC. = 0.11M

SL. NO.	NAOH ADDED (ML)	SAM. VOL. (ML)	TITRANT ADDED (ML)	TITRANT ADDED (MMOL, TOT.)	AQ. PHASE CONC. (MG/L)	AQ. PHASE CONC. (MMOL/L(M))	RESIN UPTAKE (MMOL)	RESIN UPTAKE (MMOL/GM(MR))	*MR/M	V	V/M
1	.25	5.0	5.0	.952E-02	.770E+00	.121E-01	.340E-02	.640E-03	.528E-01	1.84×10^{-4}	15.2
2	.30	5.0	5.0	.190E-01	.137E+01	.216E-01	.826E-02	.155E-02	.721E-01		
3	.30	5.0	5.0	.286E-01	.196E+01	.308E-01	.131E-01	.247E-02	.801E-01	7.1×10^{-4}	22.9
4	.20	5.0	5.0	.381E-01	.230E+01	.362E-01	.200E-01	.376E-02	.104E+00		
5	.70	10.0	10.0	.571E-01	.304E+01	.478E-01	.329E-01	.620E-02	.130E+00	1.77×10^{-3}	37

6	1.00	10.0	10.0	.7626E-01	.3876+01	.6096-01	.4576-01	.8596-02	.1416+00				
7	1.00	10.0	10.0	.9526-01	.4716+01	.7416-01	.5816-01	.1096-01	.1476+00	$3.13x10^{-3}$	42.2		
8	.80	10.0	10.0	.1146+00	.5326+01	.8376-01	.7236-01	.1306-01	.1636+00				
9	1.10	10.0	10.0	.1336+00	.6136+01	.9656-01	.8506-01	.1606-01	.1666+00	$4.6x10^{-3}$	47.5		
10	.60	10.0	10.0	.1526+00	.7036+01	.1116+00	.9706-01	.1826-01	.1656+00				
11	.50	5.0	5.0	.1626+00	.7216+01	.1136+00	.1066+00	.1996-01	.1756+00	$5.7x10^{-3}$	50.6		
12	.50	5.0	5.0	.1716+00	.7636+01	.1206+00	.1116+00	.2096-01	.1746+00				
13	.40	5.0	5.0	.1816+00	.8046+01	.1276+00	.1186+00	.2216-01	.1756+00	$6.4x10^{-3}$	50.1		
14	.60	5.0	5.0	.1906+00	.8216+01	.1296+00	.1266+00	.2376-01	.1836+00				
15	.55	5.0	5.0	.2006+00	.8436+01	.1336+00	.1346+00	.2516-01	.1896+00	$7.2x10^{-3}$	54.4		
16	.60	5.0	5.0	.2096+00	.9026+01	.1426+00	.1386+00	.2606-01	.1836+00				
17	.45	5.0	5.0	.2196+00	.9476+01	.1496+00	.1446+00	.2726-01	.1626+00	$7.8x10^{-3}$	52.1		
18	.40	5.0	5.0	.2296+00	.9966+01	.1576+00	.1506+00	.2826-01	.1806+00				
19	.35	5.0	5.0	.2346+00	.1036+02	.1626+00	.1576+00	.2966-01	.1836+00	$8.5x10^{-3}$	52.3		
20	.40	5.0	5.0	.2486+00	.1056+02	.1656+00	.1656+00	.3116-01	.1896+00				
21	.30	5.0	5.0	.2576+00	.1106+02	.1726+00	.1716+00	.3216-01	.1866+00	$9.2x10^{-3}$	53.6		
22	.50	5.0	5.0	.2676+00	.1146+02	.1796+00	.1776+00	.3336-01	.1856+00				
23	.30	5.0	5.0	.2766+00	.1196+02	.1806+00	.1826+00	.3436-01	.1026+00	$9.8x10^{-3}$	52.2		

24	.30	5.0	5.0	.2956+00	.1406+02	.2206+00	.1856+00	.3476-01	.1586+00		
25	.50	5.0	5.0	.3056+00	.1486+02	.2336+00	.1886+00	.3546-01	.1526+00	1.04×10^{-2}	42.6
26	.50	5.0	5.0	.3146+00	.1556+02	.2446+00	.1926+00	.3626-01	.1486+00		
27	.40	5.0	5.0	.3246+00	.1666+02	.2616+00	.1936+00	.3636-01	.1396+00	1.09×10^{-2}	39.1
28	.40	5.0	5.0	.3436+0C	.1776+02	.2796+00	.2026+00	.3806-01	.1366+00		
29	.20	10.0	10.0	.3626+00	.1866+02	.2936+00	.2156+00	.4056-01	.1386+00	1.2×10^{-2}	38.1
30	.50	10.0	10.0	.3826+00	.1976+02	.3156+00	.2236+00	.4206-01	.1336+00		
31	.60	10.0	10.0	.3816+00	.2006+02	.3156+00	.2236+00	.4206-01	.1336+00		
32	.60	10.0	10.0	.4006+00	.2066+02	.3246+00	.2386+00	.4476-01	.1386+00	1.34×10^{-2}	39.2
33	.50	10.0	10.0	.4196+00	.2176+02	.3426+00	.2486+00	.4676-01	.1376+00		
34	.50	10.0	10.0	.4386+00	.2256+02	.3546+00	.2616+03	.4916-01	.1396+00	1.41×10^{-2}	36
35	.40	10.0	10.0	.4576+00	.2496+02	.3926+00	.2616+00	.4916-01	.1256+00		
36	.50	10.0	10.0	.4766+00	.2736+02	.4306+00	.2616+00	.4916-01	.1146+00	1.43×10^{-2}	31.1
37	.50	10.0	10.0	.4956+00	.2926+02	.4606+00	.2656+00	.4996-01	.1096+00		
38	1.00	20.0	20.0	.5336+00	.3176+02	.4996+00	.2786+00	.5246-01	.1056+00	1.53×10^{-2}	26.6
39	1.00	20.0	20.0	.5716+00	.3666+02	.5766+00	.2836+00	.5326-01	.9246-01		
40	.80	20.0	20.0	.6096+00	.3986+02	.6266+00	.2966+00	.5566-01	.8886-01	1.68×10^{-2}	25.1
41	.90	20.0	20.0	.6476+00	.4266+02	.6706+00	.3126+00	.5866-01	.8756-01	1.75×10^{-2}	24.3
42	.80	20.0	20.0	.6866+00	.4576+02	.7196+00	.3256+00	.6126-01	.8516-01		

Appendix O

TITRATION OF BIO-REX 70 WITH COPPER AT pH 5.5 WITH 0.048M SODIUM NITRATE

WT. OF RESIN TAKEN = 1.79170

ORIGINAL TITRATION SYSTEM VOL.,ML. = 500.00000

CONCENTRATION OF TITRANT = 800.000 AS CU IN MG/LIT

BACKGROUND NANO3 CONC. = 0.048M

SL. NO.	NAOH ADDED (ML)	SAM. VOL. (ML)	TITRANT ADDED (ML)	TITRANT ADDED (MMOL, TOT.)	AQ. PHASE CONC. (MG/L)	AQ. PHASE CONC. (MMOL/L(M))	RESIN UPTAKE (MMOL)	RESIN UPTAKE (MMOL/GM(MR))	MR/M	V	V/M
1	.03	10.0	10.0	.126E+00	.250E+00	.393E-02	.124E+00	.692E-01	.176E+02	1.98×10^{-2}	5038
2	3.12	10.0	10.0	.252E+00	.270E+00	.425E-02	.250E+00	.139E+00	.328E+02	4×10^{-2}	9388
3	4.51	10.0	10.0	.378E+00	.700E+00	.110E-01	.372E+00	.208E+00	.189E+02	5.94×10^{-2}	5400
4	6.00	20.0	10.0	.504E+00	.124E+01	.195E-01	.494E+00	.276E+00	.141E+02	7.9×10^{-2}	4046
5	5.70	10.0	10.0	.630E+00	.217E+01	.342E-01	.613E+00	.342E+00	.100E+02	9.8×10^{-2}	2863
6	5.80	20.0	10.0	.755E+00	.334E+01	.526E-01	.729E+00	.407E+00	.774E+01	0.12	2205

7	5.51	10.0	10.0	.8816+00	.5226+01	.8226-01	.8416+00	.4696+00	.5716+01	0.13	1636
8	4.51	20.0	10.0	.1016+01	.9176+01	.1446+00	.9346+03	.5226+00	.3616+01	0.15	1035
9	4.32	20.0	10.0	.1136+01	.1446+02	.2276+00	.1026+01	.9706+00	.2516+01	0.16	718
10	5.11	10.0	10.0	.1266+01	.1746+02	.2746+00	.1126+01	.6276+00	.2296+01	0.18	653
11	6.70	30.0	20.0	.1516+01	.3216+02	.5056+00	.1256+01	.6986+03	.1386+01	0.2	394
12	5.71	20.0	20.0	.1766+01	.4556+02	.7166+00	.1416+01	.7866+00	.1106+01	0.23	314
13	12.01	30.0	20.0	.2016+01	.4546+02	.7156+00	.1656+01	.9206+00	.1296+01	0.26	349
14	3.10	20.0	20.0	.2276+01	.6686+02	.1056+01	.1756+01	.9766+00	.9206+03	0.28	263
15	2.50	20.0	20.0	.2526+01	.9026+02	.1426+01	.1806+01	.1016+01	.7106+00	0.29	204
16	2.80	30.0	20.0	.2776+01	.1146+03	.1796+01	.1876+01	.1046+01	.5846+00	0.3	168
17	2.85	20.0	20.0	.3026+01	.1316+03	.2076+01	.2006+01	.1126+01	.5406+00	0.32	154
18	3.73	20.0	20.0	.3276+01	.1466+03	.2296+01	.2126+01	.1186+01	.5156+00	0.34	148
19	1.29	20.0	20.0	.3536+01	.1696+03	.2666+01	.2196+01	.1226+01	.4616+00	0.35	132
20	.91	20.0	20.0	.3786+01	.1906+03	.2956+01	.2266+01	.1276+01	.4256+00	0.36	122
21	6.29	20.0	20.0	.4036+01	.2086+03	.3276+01	.2376+01	.1326+01	.4046+00	0.38	114
22	.67	20.0	20.0	.4286+01	.2306+03	.3626+01	.2476+01	.1386+01	.3616+00	0.4	104
23	2.00	30.0	30.0	.4666+01	.2616+03	.4116+01	.2956+01	.1426+01	.3466+00	0.41	99

Appendix P
TITRATION OF BIO-REX 70 WITH COPPER AT pH 5.5 WITH 0.11M SODIUM NITRATE

WT. OF RESIN TAKEN = 1.60000

ORIGINAL TITRATION SYSTEM VOL.,ML. = 500.00000

CONCENTRATION OF TITRANT = 630.000 AS CU IN MG/LIT

BACKGROUND NANO3 CONC. = 0.11M

SL. NO.	NAOH ADDED (ML)	SAM. VOL. (ML)	TITRANT ADDED (ML)	TITRANT ADDED (MMOL,TOT.)	AQ. PHASE CONC. (MG/L)	AQ. PHASE CONC. (MMOL/L(M))	RESIN UPTAKE (MMOL)	RESIN UPTAKE (MMOL/GM(MR))	MR/M	V	V/M
1	4.70	5.0	5.0	.496E-01	.800E-01	.126E-02	.489E-01	.306E-01	.243E+02	8.75×10^{-3}	6944
2	2.60	10.0	5.0	.992E-01	.140E+00	.220E-02	.980E-01	.613E-01	.278E+02	1.75×10^{-2}	7955
3	7.40	15.0	5.0	.149E+00	.200E+00	.315E-02	.147E+00	.920E-01	.292E+02		
4	4.55	10.0	5.0	.198E+00	.300E+00	.472E-02	.196E+00	.122E+00	.259E+02	3.5×10^{-2}	7415

5	7.20	10.0	5.0	.248E+00	.410E+00	.645E-02	.245E+00	.153E+00	.237E+02	4.4×10^{-2}	6791
6	7.35	15.0	5.0	.297E+00	.650E+00	.102E-01	.292E+00	.183E+00	.179E+02	5.3×10^{-2}	5177
7	8.25	15.0	5.0	.347E+00	.830E+00	.131E-01	.341E+00	.213E+00	.163E+02	6.1×10^{-2}	4657
8	8.30	10.0	5.0	.397E+00	.106E+01	.167E-01	.388E+00	.243E+00	.145E+02	6.9×10^{-2}	4156
9	6.75	15.0	5.0	.446E+00	.162E+01	.255E-01	.433E+00	.271E+00	.106E+02	7.8×10^{-2}	3039
10	7.50	15.0	5.0	.496E+00	.203E+01	.319E-01	.480E+00	.300E+00	.939E+01	8.6×10^{-2}	2693
11	7.20	10.0	5.0	.545E+00	.270E+01	.425E-01	.524E+00	.328E+00	.771E+01	9.4×10^{-2}	2205
12	8.00	15.0	5.0	.595E+00	.323E+01	.508E-01	.569E+00	.356E+00	.700E+01	0.102	2008
13	8.25	15.0	5.0	.644E+00	.385E+01	.606E-01	.614E+00	.384E+00	.634E+01	0.11	1815
14	17.15	25.0	5.0	.694E+00	.237E+01	.373E-01	.675E+00	.422E+00	.113E+02	0.12	3217
15	4.00	10.0	5.0	.744E+00	.367E+01	.578E-01	.716E+00	.447E+00	.774E+01	0.13	2249
16	5.10	10.0	5.0	.793E+00	.506E+01	.796E-01	.753E+00	.471E+00	.591E+01	0.14	1822

17	6.10	10.0	5.0	.843E+00	.646E+01	.102E+00	.792E+00	.495E+00	.487E+01	0.142	1392
18	9.75	20.0	10.0	.942E+00	.105E+02	.164E+00	.858E+00	.536E+00	.326E+01	0.153	933
19	10.00	20.0	10.0	.104E+01	.157E+02	.247E+00	.918E+00	.573E+00	.232E+01	0.164	664
20	9.50	20.0	10.0	.114E+01	.205E+02	.323E+00	.979E+00	.612E+00	.190E+01	0.175	542
21	9.35	20.0	10.0	.124E+01	.256E+02	.403E+00	.104E+01	.649E+00	.161E+01	0.186	462
22	8.80	15.0	10.0	.134E+01	.310E+02	.488E+00	.110E+01	.684E+00	.140E+01	0.197	404
23	8.50	20.0	10.0	.144E+01	.367E+02	.578E+00	.115E+01	.717E+00	.124E+01	0.206	356
24	8.50	20.0	10.0	.154E+01	.428E+02	.674E+00	.120E+01	.751E+00	.111E+01	0.215	319
25	18.10	30.0	10.0	.164E+01	.381E+02	.600E+00	.133E+01	.832E+00	.139E+01	0.238	397
26	4.50	15.0	10.0	.174E+01	.462E+02	.727E+00	.138E+01	.864E+00	.119E+01	0.247	340
27	4.50	15.0	10.0	.183E+01	.537E+02	.845E+00	.141E+01	.883E+00	.104E+01	0.252	298
28	4.60	15.0	10.0	.193E+01	.617E+02	.971E+00	.145E+01	.905E+00	.932E+00	0.26	268
29	7.30	25.0	20.0	.213E+01	.783E+02	.123E+01	.150E+01	.938E+00	.761E+00	0.27	218
30	6.00	25.0	20.0	.233E+01	.939E+02	.148E+01	.159E+01	.994E+00	.672E+00	0.28	192
31	6.20	25.0	20.0	.253E+01	.112E+03	.176E+01	.165E+01	.103E+01	.586E+00	0.295	168
32	6.65	25.0	20.0	.273E+01	.126E+03	.198E+01	.173E+01	.108E+01	.547E+00	0.31	156
33	6.41	25.0	20.0	.292E+01	.139E+03	.219E+01	.182E+01	.114E+01	.520E+00	0.33	148
34	6.60	30.0	20.0	.312E+01	.151E+03	.238E+01	.193E+01	.121E+01	.507E+00	0.35	145
35	6.40	25.0	20.0	.332E+01	.164E+03	.258E+01	.204E+01	.127E+01	.493E+00	0.37	142
36	6.00	25.0	20.0	.352E+01	.177E+03	.279E+01	.212E+01	.133E+01	.476E+00	0.38	136
37	5.80	25.0	20.0	.372E+01	.188E+03	.296E+01	.224E+01	.140E+01	.473E+00	0.4	135
38	5.25	25.0	20.0	.392E+01	.199E+03	.313E+01	.235E+01	.147E+01	.469E+00	0.42	134
39	5.90	30.0	20.0	.411E+01	.210E+03	.330E+01	.246E+01	.154E+01	.466E+00	0.44	133
40	5.45	25.0	20.0	.431E+01	.219E+03	.345E+01	.261E+01	.163E+01	.472E+00	0.47	135

Appendix Q
TITRATION OF VERGIN BIO-REX 70 WITH SODIUM SULFATE AT pH 4.0

WT. OF RESIN TAKEN = 2.95500

ORIGINAL TITRATION SYSTEM VOL.,ML. = 500.00000

CONCENTRATION OF TITRANT = 1046.500 AS SO4 IN MG/LIT

BACKGROUND NO3- CONCENTRATION = AS REQUIRED (ONLY TO MAINTAIN PH AT 4.0)

SL. NO.	NAOH ADDED (ML)	SAM. VOL. (ML)	TITRANT ADDED (ML)	(MMOL, TOT.)	AQ. PHASE CONC. (MG/L)	(MMOL/L(M))	RESIN UPTAKE (MMOL)	(MMOL/GM(MR)
1	.00	50.0	50.0	.545E+00	.884E+02	.921E+00	.388E-01	.131E-01
2	.00	50.0	50.0	.109E+01	.180E+03	.187E+01	.155E+00	.525E-01
3	.00	50.0	50.0	.164E+01	.256E+03	.266E+01	.303E+00	.102E+00
4	.00	50.0	50.0	.218E+01	.327E+03	.341E+01	.476E+00	.161E+00
5	.00	50.0	50.0	.273E+01	.393E+03	.410E+01	.677E+00	.229E+00
6	.00	50.0	50.0	.327E+01	.458E+03	.478E+01	.883E+00	.299E+00
7	.00	50.0	50.0	.382E+01	.500E+03	.521E+01	.121E+01	.410E+00
8	.00	50.0	50.0	.436E+01	.558E+03	.581E+01	.145E+01	.492E+00

Appendix R
TITRATION OF VERGIN BIO-REX 70 WITH SODIUMSULFATE AT pH 5.5

WT. OF RESIN TAKEN = 3.15220

ORIGINAL TITRATION SYSTEM VOL.,ML. = 500.00000

CONCENTRATION OF TITRANT = 1635.600 AS SO4 IN MG/LIT

BACKGROUND NO3- CONCENTRATION = AS REQUIRED (ONLY TO MAINTAIN PH)

SL. NO.	NAOH ADDED (ML)	SAM. VOL. (ML)	TITRANT ADDED (ML)	(MMOL, TOT.)	AQ. PHASE CONC. (MG/L)	(MMOL/L(M))	RESIN UPTAKE (MMOL)	(MMOL/GM(MR)
1	5.30	50.0	50.0	.852E+00	.146E+03	.152E+01	.102E-01	.325E-02
2	19.00	75.0	50.0	.170E+01	.273E+03	.285E+01	.226E+00	.718E-01
3	8.31	50.0	50.0	.256E+01	.387E+03	.403E+01	.609E+00	.193E+00
4	1.21	50.0	50.0	.341E+01	.500E+03	.521E+01	.797E+00	.253E+00
5	1.38	50.0	50.0	.426E+01	.605E+03	.630E+01	.110E+01	.349E+00
6	1.00	50.0	50.0	.511E+01	.693E+03	.722E+01	.149E+01	.474E+00
7	1.30	50.0	50.0	.596E+01	.784E+03	.817E+01	.187E+01	.593E+00

NOTE: COL 2 TO BE READ AS HNO3 ADDED INSTEAD OF NAOH ADDED

Appendix S
TITRATION OF COPPER LOADED BIO-REX 70 WITH SODIUM SULFATE AT pH 4.0

WT. OF RESIN TAKEN = 3.68200

ORIGINAL TITRATION SYSTEM VOL.,ML. = 500.00000

CONCENTRATION OF TITRANT = 1048.000 AS SO4 IN MG/LIT

BACKGROUND NANO3 CONC. = 80 MG/L(USED FOR PH ADJUSTMENT) (ONLY TO MAINTAIN PH AT 4.0)

SL. NO.	NAOH ADDED (ML)	SAM. VOL. (ML)	TITRANT ADDED (ML)	(MMOL,TOT.)	AQ. PHASE CONC. (MG/L)	(MMOL/L(M))	RESIN UPTAKE (MMOL)	(MMOL/GM(MR)
1	.00	10.0	10.0	.109E+00	.193E+02	.201E+00	.653E-02	.177E-02
2	.00	10.0	10.0	.218E+00	.402E+02	.419E+00	.880E-02	.239E-02
3	.00	10.0	10.0	.328E+00	.548E+02	.570E+00	.423E-01	.115E-01
4	.00	20.0	10.0	.437E+00	.738E+02	.769E+00	.522E-01	.142E-01
5	.00	20.0	20.0	.655E+00	.110E+03	.114E+01	.846E-01	.230E-01
6	.00	20.0	20.0	.873E+00	.144E+03	.150E+01	.122E+00	.332E-01
7	.00	20.0	20.0	.109E+01	.175E+03	.182E+01	.180E+00	.489E-01
8	.00	40.0	20.0	.131E+01	.209E+03	.218E+01	.221E+00	.600E-01
9	.00	40.0	40.0	.175E+01	.271E+03	.283E+01	.333E+00	.904E-01
10	.00	40.0	40.0	.218E+01	.323E+03	.336E+01	.502E+00	.136E+00
11	.00	40.0	40.0	.262E+01	.377E+03	.393E+01	.655E+00	.178E+00
12	.00	40.0	40.0	.306E+01	.427E+03	.445E+01	.831E+00	.226E+00

Appendix T
TITRATION OF COPPER LOADED BIO-REX 70 WITH SODIUM SULFATE AT pH 5.5

WT. OF RESIN TAKEN = 1.79170

ORIGINAL TITRATION SYSTEM VOL.,ML. = 500.00000

CONCENTRATION OF TITRANT = 1635.600 AS SO4 IN MG/LIT

BACKGROUND NO3- CONCENTRATION = AS REQUIRED (ONLY TO MAINTAIN PH)

SL. NO.	NAOH ADDED (ML)	SAM. VOL. (ML)	TITRANT ADDED (ML)	TITRANT ADDED (MMOL,TOT.)	AQ. PHASE CONC. (MG/L)	AQ. PHASE CONC. (MMOL/L(M))	RESIN UPTAKE (MMOL)	RESIN UPTAKE (MMOL/GM(MR)
1	4.60	50.0	50.0	.852E+00	.143E+03	.149E+01	.246E-01	.137E-01
2	2.37	50.0	50.0	.170E+01	.276E+03	.287E+01	.262E+00	.146E+00
3	2.25	50.0	50.0	.256E+01	.387E+03	.403E+01	.532E+00	.297E+00
4	1.99	50.0	50.0	.341E+01	.500E+03	.521E+01	.793E+00	.443E+00
5	1.85	50.0	50.0	.426E+01	.593E+03	.618E+01	.116E+01	.647E+00
6	1.27	50.0	50.0	.511E+01	.676E+03	.704E+01	.158E+01	.882E+00
7	1.32	5.0	50.0	.596E+01	.761E+03	.793E+01	.199E+01	.111E+01

NOTE: COL 2 TO BE READ AS HNO3 ADDED INSTEAD OF NAOH ADDDED

Appendix U
TITRATION OF BIO-REX 70 WITH LEAD AT pH 4.0 WITH 0.11M SODIUM NITRATE

WT. OF RESIN TAKEN = 2.50400

ORIGINAL TITRATION SYSTEM VOL.,ML. = 500.00000

CONCENTRATION OF TITRANT = 609.000 AS PB IN MG/LIT

BACKGROUND NANO3 CONC. = 0.11M

SL. NO.	NAOH ADDED (ML)	SAM. VOL. (ML)	TITRANT ADDED (ML)	(MMOL,TOT.)	AQ. PHASE CONC. (MG/L)	(MMOL/L(M))	RESIN UPTAKE (MMOL)	(MMOL/GM(MR))	MR/M	V	V/M
1	5.00	10.0	10.0	.294E-01	.163E+01	.787E-02	.253E-01	.101E-01	.129E+01	2.9×10^{-3}	368
2	4.75	20.0	10.0	.588E-01	.348E+01	.168E-01	.503E-01	.201E-01	.120E+01	5.76×10^{-3}	343
3	5.00	10.0	10.0	.882E-01	.540E+01	.261E-01	.753E-01	.301E-01	.115E+01	8.63×10^{-3}	331
4	4.75	20.0	10.0	.118E+00	.771E+01	.372E-01	.988E-01	.395E-01	.106E+01	1.13×10^{-2}	304
5	4.50	10.0	10.0	.147E+00	.100E+02	.484E-01	.123E+00	.491E-01	.102E+01	1.41×10^{-2}	291
6	4.00	20.0	10.0	.176E+00	.130E+02	.628E-01	.145E+00	.578E-01	.920E+00	1.66×10^{-2}	264
7	4.50	10.0	10.0	.206E+00	.169E+02	.816E-01	.165E+00	.661E-01	.810E+00	1.89×10^{-2}	232
8	4.00	20.0	10.0	.235E+00	.192E+02	.927E-01	.188E+00	.753E-01	.812E+00		
9	3.50	10.0	10.0	.265E+00	.235E+02	.113E+00	.209E+00	.833E-01	.734E+00	2.4×10^{-2}	212
10	3.50	10.0	10.0	.294E+00	.262E+02	.126E+00	.230E+00	.920E-01	.727E+00	2.63×10^{-2}	209
11	3.50	20.0	10.0	.323E+00	.304E+02	.147E+00	.249E+00	.996E-01	.679E+00	2.85×10^{-2}	194
12	4.50	10.0	10.0	.353E+00	.329E+02	.159E+00	.274E+00	.110E+00	.690E+00		
13	3.50	10.0	10.0	.382E+00	.371E+02	.179E+00	.292E+00	.117E+00	.651E+00		

14	3.00	20.0	10.0	.412E+00	.415E+02	.200E+00	.311E+00	.124E+00	.620E+00	3.56×10^{-2}	178
15	3.00	10.0	10.0	.441E+00	.463E+02	.223E+00	.331E+00	.132E+00	.591E+00		
16	3.00	10.0	10.0	.470E+00	.517E+02	.250E+00	.345E+00	.138E+00	.552E+00	3.95×10^{-2}	158
17	2.50	10.0	10.0	.500E+00	.568E+02	.274E+00	.362E+00	.145E+00	.527E+00		
18	2.50	20.0	10.0	.529E+00	.618E+02	.298E+00	.379E+00	.151E+00	.508E+00	4.34×10^{-2}	146
19	2.50	10.0	10.0	.558E+00	.674E+02	.325E+00	.398E+00	.159E+00	.489E+00		
20	4.00	10.0	10.0	.588E+00	.721E+02	.348E+00	.412E+00	.165E+00	.473E+00	4.72×10^{-2}	136
21	5.50	30.0	20.0	.647E+00	.779E+02	.376E+00	.453E+00	.181E+00	.481E+00		
22	4.00	20.0	20.0	.705E+00	.881E+02	.425E+00	.495E+00	.198E+00	.465E+00	5.67×10^{-2}	133
23	3.00	20.0	20.0	.764E+00	.100E+03	.483E+00	.521E+00	.208E+00	.431E+00		

24	3.50	30.0	20.0	.8234E+00	.1126E+03	.5386E+00	.5526E+00	.2206E+00	.4106E+00	6.32×10^{-2}	118	
25	3.03	20.0	20.0	.8826E+00	.1226E+03	.5896E+00	.5916E+00	.2366E+00	.4016E+00			
26	3.00	20.0	20.0	.9416E+00	.1326E+03	.6386E+00	.6206E+00	.2476E+00	.3886E+00	7.1×10^{-2}	110	
27	3.00	20.0	20.0	.9996E+00	.1426E+03	.6866E+00	.6546E+00	.2616E+03	.3816E+00			
28	3.00	30.0	20.0	.1056E+01	.1526E+03	.7346E+00	.6896E+00	.2756E+00	.3756E+00	7.89×10^{-2}	107	
29	3.00	20.0	20.0	.1126E+01	.1616E+03	.7796E+00	.7336E+00	.2936E+00	.3766E+00			
30	7.60	30.0	20.0	.1186E+01	.1756E+03	.8426E+00	.7496E+00	.2996E+00	.3556E+00	8.58×10^{-2}	102	
31	2.00	20.0	20.0	.1236E+01	.1886E+03	.9076E+00	.7886E+00	.3156E+00	.3476E+00			
32	2.00	20.0	20.0	.1296E+01	.2016E+03	.9726E+00	.8066E+00	.3226E+03	.3316E+00	9.23×10^{-2}	95	
33	2.00	20.0	20.0	.1356E+01	.2146E+03	.1036E+01	.8336E+00	.3336E+00	.3226E+00			
34	1.50	30.0	20.0	.1416E+01	.2246E+03	.1086E+01	.8696E+00	.3476E+00	.3216E+00	9.95×10^{-2}	92	
35	1.50	20.0	20.0	.1476E+01	.2396E+03	.1156E+01	.9046E+00	.3616E+00	.3146E+00			
36	1.50	20.0	20.0	.1536E+01	.2506E+03	.1216E+01	.9236E+00	.3696E+00	.3066E+00	6.106	87	

Appendix V
TITRATION OF CHELEX-100 WITH COPPER AT pH 4.0 WITH 0.11M SODIUM NITRATE

WT. OF RESIN TAKEN = 3.3150

ORIGINAL TITRATION SYSTEM VOL.,ML. = 500.00000

CONCENTRATION OF TITRANT = 363.500 AS CU IN MG/LIT

BACKGROUND NANO3 CONC. = 0.11 M

SL. NO.	NAOH ADDED (ML)	SAM. VOL. (ML)	TITRANT ADDED (ML)	(MMOL, TOT.)	AQ. PHASE CONC. (MG/L)	(MMOL/L(M))	RESIN UPTAKE (MMOL)	(MMOL/GM(MR))	MR/M	V	V/M
1	2.00	5.0	5.0	.286E-01	.300E-01	.472E-03	.284E-01	.856E-02	.181E+02		
2	2.00	5.0	5.0	.572E-01	.300E-01	.472E-03	.570E-01	.172E-01	.364E+02		
3	2.00	5.0	5.0	.858E-01	.300E-01	.472E-03	.856E-01	.258E-01	.547E+02		
4	1.80	5.0	5.0	.114E+00	.300E-01	.472E-03	.114E+00	.344E-01	.730E+02		
5	1.90	5.0	5.0	.143E+00	.300E-01	.472E-03	.143E+00	.431E-01	.912E+02		
6	9.70	10.0	10.0	.200E+00	.300E-01	.472E-03	.200E+00	.603E-01	.128E+03		
7	3.70	10.0	10.0	.257E+00	.300E-01	.472E-03	.257E+00	.776E-01	.164E+03		
8	3.80	10.0	10.0	.315E+00	.300E-01	.472E-03	.314E+00	.948E-01	.201E+03		
9	3.80	10.0	10.0	.372E+00	.300E-01	.472E-03	.372E+00	.112E+00	.237E+03		
10	3.80	10.0	10.0	.429E+00	.300E-01	.472E-03	.429E+00	.129E+00	.274E+03		
11	3.70	10.0	10.0	.486E+00	.300E-01	.472E-03	.486E+00	.147E+00	.311E+03		
12	3.70	10.0	10.0	.543E+00	.500E-01	.787E-03	.543E+00	.164E+00	.208E+03		
13	3.70	10.0	10.0	.601E+00	.700E-01	.110E-02	.600E+00	.181E+00	.164E+03		

14	3.65	10.0	10.0	.658E+00	.600E-01	.944E-03	.657E+00	.198E+00	.210E+03		
15	3.90	10.0	10.0	.715E+00	.400E-01	.630E-03	.715E+00	.216E+00	.343E+03		
16	3.40	10.0	10.0	.772E+00	.700E-01	.110E-02	.772E+00	.233E+00	.211E+03		
17	3.45	10.0	10.0	.830E+00	.150E+00	.236E-02	.828E+00	.250E+00	.106E+03		
18	3.70	10.0	10.0	.887E+00	.300E-01	.472E-03	.886E+00	.267E+00	.566E+03		
19	2.90	20.0	10.0	.944E+00	.400E-01	.630E-03	.944E+00	.285E+00	.452E+03		
20	3.10	20.0	10.0	.100E+01	.900E-01	.142E-02	.100E+01	.302E+00	.213E+03		
21	3.20	20.0	10.0	.106E+01	.100E+00	.157E-02	.106E+01	.319E+00	.203E+03		
22	3.20	20.0	10.0	.112E+01	.160E+00	.252E-02	.111E+01	.336E+00	.133E+03		
23	3.00	20.0	10.0	.117E+01	.240E+00	.378E-02	.117E+01	.353E+00	.935E+02	0.262	69400
24	3.40	20.0	10.0	.123E+01	.280E+00	.441E-02	.123E+01	.370E+00	.840E+02	0.276	62586
25	2.65	20.0	10.0	.129E+01	.330E+00	.519E-02	.128E+01	.388E+00	.746E+02	0.287	55298
26	3.00	20.0	10.0	.134E+01	.680E+00	.107E-01	.134E+01	.404E+00	.377E+02	0.3	28000
27	3.00	10.0	10.0	.140E+01	.200E+00	.315E-02	.140E+01	.422E+00	.134E+03		
28	2.25	10.0	10.0	.146E+01	.180E+00	.283E-02	.146E+01	.440E+00	.155E+03		
29	2.50	10.0	10.0	.152E+01	.380E+00	.598E-02	.151E+01	.456E+00	.763E+02	0.338	56616
30	2.75	10.0	10.0	.157E+01	.720E+00	.113E-01	.157E+01	.473E+00	.417E+02	0.352	31152
31	2.80	20.0	10.0	.163E+01	.111E+01	.175E-01	.162E+01	.489E+00	.280E+02	0.363	20756
32	2.50	10.0	10.0	.169E+01	.192E+01	.302E-01	.167E+01	.505E+00	.167E+02	0.374	12399
33	2.25	10.0	10.0	.174E+01	.268E+01	.422E-01	.172E+01	.520E+00	.123E+02	0.386	9139
34	2.00	10.0	10.0	.180E+01	.454E+01	.715E-01	.177E+01	.533E+00	.746E+01	0.397	5550
35	1.50	10.0	10.0	.186E+01	.772E+01	.121E+00	.180E+01	.542E+00	.446E+01		
36	1.25	10.0	10.0	.192E+01	.981E+01	.154E+00	.184E+01	.555E+00	.359E+01	0.413	2679
37	.75	10.0	10.0	.197E+01	.162E+02	.255E+00	.185E+01	.557E+00	.218E+01		
38	.75	10.0	10.0	.203E+01	.202E+02	.318E+00	.187E+01	.565E+00	.178E+01	0.419	1318
39	.25	20.0	10.0	.209E+01	.257E+02	.404E+00	.189E+01	.569E+00	.141E+01		

40	.35	10.0	10.0	.215E+01	.307E+02	.483E+00	.191E+01	.576E+00	.119E+01	0.428	887
41	.40	10.0	10.0	.220E+01	.355E+02	.559E+00	.192E+01	.580E+00	.104E+01		
42	.40	10.0	10.0	.226E+01	.416E+02	.655E+00	.193E+01	.583E+00	.890E+00	0.433	661
43	.30	10.0	10.0	.232E+01	.467E+02	.735E+00	.195E+01	.588E+00	.800E+00		
44	.20	10.0	10.0	.237E+01	.516E+02	.812E+00	.197E+01	.594E+00	.731E+00	0.442	544
45	.10	10.0	10.0	.243E+01	.580E+02	.913E+00	.197E+01	.596E+00	.653E+00		
46	.10	10.0	10.0	.249E+01	.640E+02	.101E+01	.198E+01	.599E+00	.594E+00	0.444	440
47	.30	10.0	10.0	.255E+01	.685E+02	.108E+01	.201E+01	.605E+00	.561E+00		
48	.20	10.0	10.0	.260E+01	.745E+02	.117E+01	.202E+01	.608E+00	.519E+00	0.453	387
49	.10	10.0	10.0	.266E+01	.789E+02	.124E+01	.204E+01	.615E+00	.495E+00		
50	.10	10.0	10.0	.272E+01	.842E+02	.133E+01	.205E+01	.620E+00	.468E+00	0.46	346
51	.00	10.0	10.0	.277E+01	.895E+02	.141E+01	.207E+01	.625E+00	.443E+00	0.464	329
52	.00	10.0	10.0	.283E+01	.947E+02	.149E+01	.209E+01	.629E+00	.422E+00	0.469	314
53	.00	10.0	10.0	.289E+01	.100E+03	.158E+01	.210E+01	.633E+00	.401E+00	0.471	298
54	.00	10.0	10.0	.295E+01	.105E+03	.165E+01	.212E+01	.640E+00	.389E+00	0.475	288
55	.00	10.0	10.0	.300E+01	.110E+03	.173E+01	.214E+01	.646E+00	.374E+00	0.48	277
56	.00	10.0	10.0	.306E+01	.115E+03	.181E+01	.215E+01	.650E+00	.358E+00	0.482	266
57	.00	10.0	10.0	.312E+01	.120E+03	.188E+01	.218E+01	.657E+00	.349E+00		
58	.10	10.0	10.0	.318E+01	.125E+03	.197E+01	.219E+01	.661E+00	.336E+00	0.491	249
59	.00	10.0	10.0	.323E+01	.130E+03	.205E+01	.221E+01	.666E+00	.325E+00		
60	.00	10.0	10.0	.329E+01	.136E+03	.214E+01	.222E+01	.670E+00	.313E+00	0.498	233

Appendix W
TITRATION OF COPPER (1000 MG/L) WITH En AT pH 4.0

Sl No.	EN added		NaOH added			Σ Meq.	Cu T	Cu T	ENT	ENT	$f = \frac{X}{Y}$	$1-f$	$\frac{\Sigma A}{Y_1}$
	ml V_1	mmol A	ml V_2	mmol B	N C	X	$\left(\frac{50 \times N \times 1000}{50+\Sigma V_1+\Sigma V_2}\right)$ mg/l	mmol/l	$\left(\frac{\Sigma A}{50+\Sigma V_1+\Sigma V_2}\right)$ mol/l	Cu T			
1.	0	0	0	0	0	0	1000	15.74	0	0	0	0	0
2.	5	0.339	3.0	0.141	0.141	0.141	862.07	13.57	5.84×10^{-3}	4.31×10^{-1}	0.0816	0.91	0.43
3.	5	0.339	2.35	0.110	0.11	0.251	765.11	12.04	0.0104	8.61×10^{-1}	0.159	0.841	0.86
4	5	0.339	1.65	0.078	0.078	0.329	694.44	10.93	0.0141	1.29	0.209	0.791	1.29
5.	5	0.339	1.45	0.068	0.068	0.397	637.35	10.03	0.0173	1.72	0.252	0.748	1.72
6.	5	0.339	1.15	0.054	0.054	0.451	591.02	9.30	0.02	2.15	0.286	0.714	2.15
7.	5	0.339	0.95	0.045	0.045	0.5	552.18	8.69	0.0225	2.58	0.318	0.682	2.58
8.	5	0.339	0.85	0.04	0.04	0.54	518.7	8.16	0.0246	3.02	0.343	0.657	3.01
9.	5	0.339	0.7	0.033	0.033	0.573	489.72	7.71	0.0265	3.45	0.364	0.636	3.44
10.	5	0.339	0.6	0.028	0.028	0.6	464.25	7.31	0.0283	3.87	0.381	0.619	3.87
11.	5	0.339	0.5	0.024	0.024	0.624	441.70	6.95	0.03	4.31	0.396	0.604	4.31
12.	5	0.339	0.4	0.019	0.019	0.643	421.59	6.63	0.0314	4.74	0.409	0.591	4.74
13.	5	0.339	0.4	0.019	0.019	0.662	403.23	6.346	0.0328	5.16	0.42	0.58	5.17
14.	5	0.339	0.35	0.0165	0.0165	0.679	386.55	6.08	0.0341	5.6	0.431	0.569	5.60
15	5	0.339	0.35	0.0165	0.0165	0.7	371.2	5.84	0.0352	6.03	0.44	0.56	6.03
16.	5	0.339	0.4	0.019	0.019	0.719	356.89	5.62	0.0363	6.46	0.457	0.543	6.46
17.	10	0.68	0.6	0.028	0.028	0.747	331.79	5.22	0.0383	7.33	0.474	0.526	7.32
18.	10	0.68	0	0	0	0.747	311.14	4.897	0.0401	8.19	0.474	0.526	8.18
19	10	0.68	0.6	0.028	0.028	0.775	291.89	4.594	0.0416	9.05	0.492	0.508	9.04
20	10	0.68	0.25	0.012	0.012	0.787	275.41	4.33	0.043	9.93	0.5	0.5	9.90

NOTE: En Conc. = 4072 mg/l ; NaOH Conc. = 0.0471 N.

Appendix X
TITRATION OF COPPER (100 MG/L) WITH En AT pH 4.0

Sl No.	En added		NaOH added			ΣM_{av}	Cu^{++} $\left(\frac{5\times1000}{50+\Sigma V_1+\Sigma V_2}\right)$ mg/l.	Cu^{++} mmol/l.	Ent $\frac{\Sigma A}{(50+\Sigma V_1+\Sigma V_2)}$ mol/l.	Ent/Cu^{++}	$f=\frac{x}{y}$	$1-f$	$\Sigma A/Y_1$
	ml V_1	mmol A	ml V_2	mmol B	mmol C	X							
1	0	0	0	0	0	0	100	1.574	0	0	0	0	0
2.	5	0.339	0.33	0.0155	0.0155	0.0155	90.37	1.422	6.13×10^{-3}	4.31	0.099	0.9	4.3
3	5	0.339	0.28	0.0132	0.0132	0.0287	82.49	1.3	1.12×10^{-2}	8.6	0.183	0.817	8.6
4.	5	0.339	0.22	0.0103	0.0103	0.039	75.95	1.195	1.54×10^{-2}	1.29×10	0.248	0.752	12.9
5.	5	0.339	0.13	0.0061	0.0061	0.0452	70.46	1.11	1.91×10^{-2}	1.72×10	0.288	0.712	17.2
6.	5	0.339	0.13	0.0061	0.0061	0.0513	65.71	1.034	2.23×10^{-2}	2.15×10	0.327	0.673	21.5
7.	5	0.339	0.1	0.0047	0.0047	0.056	61.58	0.969	2.51×10^{-2}	2.58×10	0.357	0.643	25.8
8	5	0.339	0.08	0.0037	0.0037	0.0598	57.96	0.912	2.75×10^{-2}	3.01×10	0.321	0.619	30.1
9	5	0.339	0.06	0.0028	0.0028	0.063	54.75	0.862	2.97×10^{-2}	3.44×10	0.401	0.599	34.4
10	5	0.339	0.06	0.0028	0.0028	0.066	51.87	0.816	3.16×10^{-2}	3.88×10	0.42	0.58	38.7
11	5	0.339	0.05	0.0024	0.0024	0.0684	49.29	0.776	3.34×10^{-2}	4.31×10	0.436	0.564	43.1
12.	5	0.339	0.06	0.0028	0.0028	0.071	46.95	0.739	3.5×10^{-2}	4.74×10	0.452	0.548	47.4
13	5	0.339	0.04	0.00188	0.00188	0.073	44.83	0.705	3.65×10^{-2}	5.17×10	0.465	0.535	51.7
14	5	0.339	0.04	0.00188	0.00188	0.075	42.89	0.675	3.78×10^{-2}	5.6×10	0.48	0.52	56.0
15	5	0.339	0.03	0.0014	0.0014	0.0764	41.12	0.647	3.91×10^{-2}	6.03×10	0.49	0.51	60.3

NOTE: En Conc.= 4072 mg/l ; NaOH Conc.= 0.0471 N

Appendix Y
THEORETICAL CALCULATIONS FOR THE TITRATION OF COPPER WITH En AT pH 4.0

A. BASIC EQUATIONS INVOLVED IN THE TITRATION

$$En + H^+ = EnH^+ \quad , K_{ST1}' \qquad (1)$$

$$EnH^+ + H^+ = EnH_2^{2+} \quad , K_{ST2}' \qquad (2)$$

$$Cu^{2+} + En = Cu(En)^{2+} \quad , K_{ST1} = 10^{10.54} \qquad (3)$$

$$Cu(En)^{2+} + En = Cu(En)_2^{2+} \quad , K_{ST2} = 10^{9.06} \qquad (4)$$

Note : K_{ST1} and K_{ST2} of Eq. (3) and (4) above are at ionic strength (U) = 0.1 at 25^oC

$$Cu^{2+} + Cu(En)^{2+} + Cu(En)_2^{2+} = Cu_T \qquad (5)$$

$$En + EnH^+ + EnH_2^{2+} + Cu(En)^{2+} + 2*Cu(En)_2^{2+} = En_T \qquad (6)$$

Note : For the titration conditions $Cu_T = 13.57 \times 10^{-3}$ mol/l and $En_T = 4.31 \times 10^{-1}$ mol/l.

From Eq. (1) above,

$$K_{ST1} = \frac{\{EnH^+\}}{\{En\}\{H^+\}} = \frac{Y_1\ [EnH^+]}{[En][H^+]} = Y_1 * K_{ST1}'$$

From Eq. (2) above,

$$K_{ST2} = \frac{\{EnH_2^{2+}\}}{\{EnH^+\}\{H^+\}} = \frac{Y_2\ [EnH_2^{2+}]}{Y_1[EnH^+][H^+]} = \frac{Y_2}{Y_1} * K_{ST2}'$$

For the reactions 1 and 2 above, K_{ST1} and K_{ST2} are $10^{9.928}$ and $10^{6.848}$ respectively at U = 0 and at 25°C

Now, for the titration system with about 1000 mg/l copper and 0.11M sodium nitrate, the following calculations can be made.

Species	Concentration(C) (mol/l)	Charge(Z)	CZ^2
Na^+	0.11	1	0.11
NO_3^-	0.11	1	0.11
Cu^{2+}	13.57×10^{-3}	2	54.28×10^{-3}

NO_3^-	27.14×10^{-3}	1	27.14×10^{-3}

Total CZ^2 = 0.301

Therefore, ionic strength $U = 0.5 \times (\text{sum } CZ^2) = 0.151$

$$\text{Activity coefficient } \log Y_1 = -0.5\, Z^2 \frac{(\text{ROOT } U)}{1 + (\text{ROOT } U)}$$

For species with charge 1, $\log Y_1 = -0.317$

Therefore, $Y_1 = 0.482$

and $Y_2 = Y_1^4 = 5.39 \times 10^{-2}$

For all the titration points, the following computaional table is made to correct the stability constants (K_{ST1} and K_{ST2}) for the ionic strength effect into the corrected stability constant (K_{ST1}' AND K_{ST2}')

Cu(II) Conc. MOL/L	Ionic Strength(U)	Y_1	Y_2	K_{ST1}'	K_{ST2}'
13.57×10^{-3}	0.151	0.482	0.054	1.76×10^{10}	6.31×10^{7}
10.93×10^{-3}	0.143	0.497	0.061	1.70×10^{10}	5.74×10^{7}
9.30×10^{-3}	0.138	0.506	0.066	1.67×10^{10}	5.42×10^{7}
8.16×10^{-3}	0.134	0.513	0.069	1.65×10^{10}	5.21×10^{7}
7.31×10^{-3}	0.132	0.519	0.072	1.63×10^{10}	5.05×10^{7}
6.63×10^{-3}	0.13	0.523	0.075	1.62×10^{10}	4.93×10^{7}

$6.08X10^{-3}$	0.128	0.526	0.076	$1.61X10^{10}$	$4.84X10^{7}$
$5.62X10^{-3}$	0.127	0.529	0.078	$1.60X10^{10}$	$4.76X10^{7}$
$4.90X10^{-3}$	0.125	0.533	0.081	$1.59X10^{10}$	$4.64X10^{7}$
$4.33X10^{-3}$	0.122	0.537	0.083	$1.58X10^{10}$	$4.55X10^{7}$

For the titration of second set of titration with 100 mg/l of copper with 0.11 M sodium nitrate the corrected stability constants of reactions 1 and 2 are as follows:

$1.42x10^{-3}$	0.114	0.555	0.095	$1.53x10^{10}$	$4.11x10^{7}$
$1.20x10^{-3}$	0.114	0.557	0.096	$1.52x10^{10}$	$4.08x10^{7}$
$1.03x10^{-3}$	0.113	0.558	0.097	$1.52x10^{10}$	$4.06x10^{7}$
$0.91x10^{-3}$	0.113	0.56	0.098	$1.52x10^{10}$	$4.04x10^{7}$
$0.82x10^{-3}$	0.112	0.56	0.098	$1.51x10^{10}$	$4.03x10^{7}$
$0.74x10^{-3}$	0.112	0.56	0.098	$1.51x10^{10}$	$4.01x10^{7}$
$0.68x10^{-3}$	0.112	0.56	0.099	$1.51x10^{10}$	$4.00x10^{7}$

VITA

Tushar K. Roy, born in January 1954 at Calcutta, received his Bachelor of Chemical Engineering degree, with First Class Honours, in the year 1976 from the Jadavpur University at Calcutta, India. Tushar Roy worked in the industry from July 1976 to December 1986 in the field of water and industrial waste effluent treatment before coming to Lehigh University for graduate study in Environmental Engineering. Tushar Roy, along with his academic advisor and others, has published and presented the following papers.

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